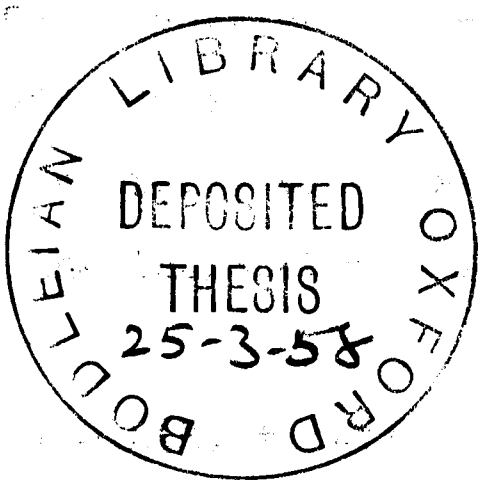
Thermochemical and Spectroscopic Studies of Bond Energies in Simple Molecules

Abstract of a Thesis presented
for the Degree of D.Phil.
in the University of Oxford



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ABSTRACT

The gaseous alkali halide molecules are of interest because they constitute a group particularly susceptible to theoretical interpretation. It does not seem to be too far from the truth to regard them as systems of simple polarizable ions.[1,2]

An important molecular property is the dissociation energy, D(MX). In the case of the alkali halides, this may be determined either by spectroscopic or by thermochemical methods. However, although analyses of their ultraviolet absorption spectra have given fair estimates of the dissociation energies[3], the method of analysis is here liable to systematic errors and is best used to get relative values.[4] The most reliable estimates of the energies of dissociation are therefore to be obtained from the thermochemical cycle which may be written

$$D(MX) = - Q_f(MX) - \Delta_s H(MX) + \Delta_s H(M) + \tfrac{1}{2}D(X_2) \ldots\ldots (1)$$

The quantities least well known in equations (1) for the alkali halides are often the heats of sublimation, $\Delta_s H_{298}(MX)$, of the salts. There is at present available in several cases information only on the vapour pressure above the liquids at relatively high temperatures, and the corrections to give $\Delta_s H_{298}$ are large and uncertain, and more so since the only values

commonly known for the heats of fusion are derived from rather scanty information on freezing points in binary systems.[5]

On these grounds, the merits of determining $\Delta_s H_{298}$ by measuring the vapour pressures above the crystal at relatively low temperatures are obvious, in addition it has recently become clear that the interpretation of measurements at higher pressures is not simple. There is now good evidence, both from electron impact studies,[6] and from the observations of molecular beams,[7] that the vapours of the alkali halides consist by no means exclusively of monomers, MX, but also contain appreciable proportions of polymers, especially of $(MX)_2$. It would be expected that at the low vapour pressures obtaining above the crystal, dimerisation would be relatively unimportant, and that reliable values of $\Delta_s H_{298}$ for the monomeric species might be obtained by simple treatments. In fact, the results given below may be taken to indicate that this is the situation for caesium and rubidium fluorides, but that in lithium, sodium, and, to a larger extent in potassium fluorides, dimerisation is significant even at pressures in the range 10^{-4} to 10^{-2} mm.

EXPERIMENTAL

Apparatus

The vapour pressures were determined by the torsion-fibre effusion method described by Barrow *et al.*[8] However it was necessary to work at considerably higher temperatures, and a new and somewhat different apparatus was constructed. The effusion vessel was contained in a translucent silica tube, closed at the bottom and provided with a flange at the top. Surrounding the tube was a furnace wound with resistance wire in four sections through which the current could be independently controlled. The distribution of temperature inside the tube was thoroughly explored in a series of preliminary experiments. Chromel-P-Alumel thermo-couples, calibrated at the freezing-points of zinc, aluminium and silver were used. The effusion vessel itself hung in a constant temperature enclosure formed by radiation shields. The furnace was fitted with counterweights, and loading of the effusion vessel was accomplished by withdrawing the furnace and breaking the flange joint on to a water-cooled brass flange which carried the support for the quartz fibre. Angles of twist of the fibre were measured on a circular perspex scale which extended over about 110°. Movement of the effusion vessel could be damped magnetically. A radioactive source minimised the effects of stray electrostatic charges. The whole apparatus was mounted on supports designed to damp

vibrations transmitted through the laboratory floor, and was insulated from the rotary oil-pump. Residual pressures within the apparatus were measured on an ionization gauge: in satisfactory operation these were less than 10^{-5} mm. Hg.

Experiments to test the absolute calibration of the apparatus were carried out with potassium chloride in a silica effusion vessel. The fluorides, however, react with silica at high temperatures, and graphite vessels[9] were first used. Although a great deal of effort was expended, it proved impossible to obtain consistent results with them. It was finally concluded that graphite is unsuitable for this purpose, first because it is difficult to free from magnetic impurities, and second because of its capacity for adsorption. A platinum vessel was then obtained whose behaviour was entirely satisfactory.

Materials.

Lithium fluoride of the highest purity is used for windows in vacuum ultraviolet spectroscopy. A sample was prepared by powdering a fragment of broken window.

The remaining alkali metal fluorides were prepared by adding a very slight excess of dilute hydrofluoric acid to the carbonate (of Analar quality or better) in a platinum dish, evaporating to dryness and heating the residue strongly to decompose any bifluoride present. Caesium bifluoride, the most

stable bifluoride, is said to be completely dissociated at 500 to 600°C.[10]

In the case of potassium chloride, a commercial sample of Analar reagent was used.

Calibration.

Several concordant determinations of the vapour pressure of solid potassium chloride have been made, and it was initially intended to use this substance for calibration of the new apparatus in the way that zinc was used in earlier work, and a number of runs were in fact done with different vessels. The thermal Estimates of $\Delta_s H_{298}$ for potassium chloride obtained from the second law Σ -equations were found to lie slightly but significantly higher than those calculated from the third law expression[26] $\Delta H^\circ = T(S^\circ_g - R\ln P - S^\circ_c)$. In view of the difficulty of treating the dimerisation in the vapour exactly, it was decided to rely on absolute, rather than relative calibration.

TABLE I

Sub-stance	A	B	Temp. °K	$\Delta_s H_{298}$ second law	kcal/mole third law
KCl			819-945	53.92 + 0.15	52.7
LiF	14697	11.567	1001-1123	70.37 + 0.73	64.8
NaF	14350	10.811	1023-1166	68.91 + 0.99	67.1
KF	12275	10.499	902-1023	58.97 + 0.47	57.6
RbF	11551	10.527	853-960	55.64 + 0.65	54.8
CsF	10208	10437	754-856	48.73 + 1.02	49.1

$$\text{Log } p(\text{mm}) = -\frac{A}{T} + B$$

Thermal data were taken from Kubachewski and Evans[12] and recent literature.[12, 14, 15, 16, 17.]

The equilibrium pressure, p, is related to the angle of twist θ by $p = k\theta$, where $k = 2/C(a_1f_1x_1 + a_2f_2x_2)$: C is the torsion constant of the fibre, a_1 and a_2 are the areas of effusion holes at distances x_1 and x_2 from the axis, and f_1 and f_2 are factors depending on the depth of the holes. Having determined k, the readings of θ obtained for potassium chloride were converted into values of the pressure. The results are illustrated in figure 1 where they are compared with the observations of other workers. The agreement is generally good, both in respect of the absolute magnitude of the pressure and in the slope of the graph of log p against 1

RESULTS AND DISCUSSION

The results of the present experiments are summarised in table 1; The most striking feature is the extent of the disagreement between the results of the second and third law calculations of $\Delta_s H_{298}$ for lithium fluoride (table 3); the second law result is no less than 5.5 Kcal higher than the third law value. This unusual discrepancy i confirmed by less reliable results obtained with graphite effusion vessels. The same trend is observed for other halides, although to a smaller extent, while for rubidium and caesium fluorides the second and third law estimates agree to within the expected limits of error.

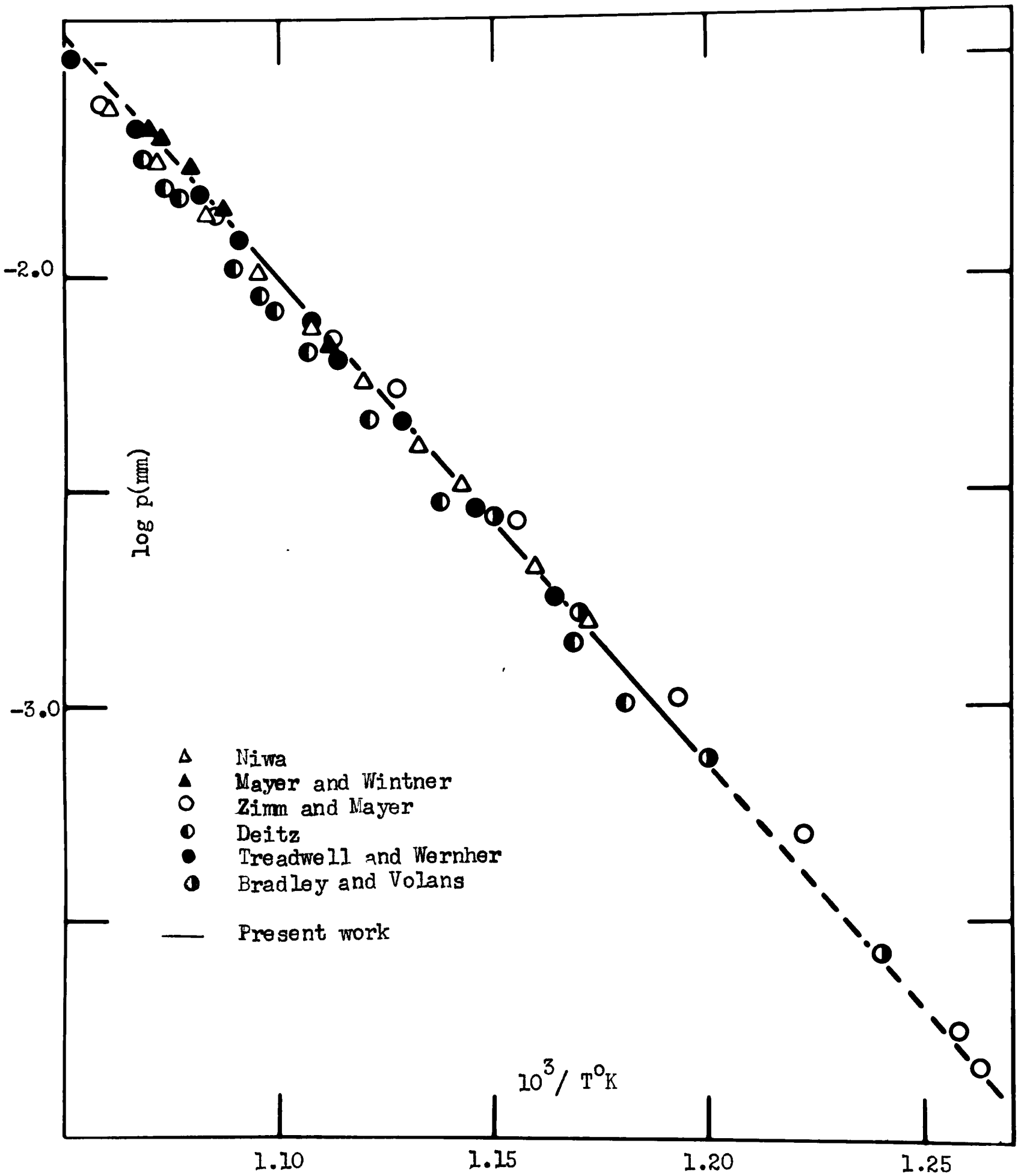
-2.0
-3.0
log p(mm)
Niwa
Mayer and Wintner
Zimm and Mayer
Deitz
Treadwell and Wernher
Bradley and Volans
Present work
10^3/ T°K
1.10
1.15
1.20
1.25

Fig. 1

These discrepancies can largely be reconciled if account is taken of dimerisation in the gas phase. That the gaseous alkali halides consist not only of monomeric species has been demonstrated in particular by Friedman[6] and by Miller and Kusch[7]. Friedman carried out a mass-spectrometric study of the vapour in equilibrium with lithium iodide in the temperature range 633 to 758°K and found not only the expected ions, LiI^+, Li^+ and I^+, but also Li_2I^+: the relative intensities indicated roughly equal proportions of LiI and Li_2I_2 in the gas. Molecular beam magnetic resonance observations[24] had earlier given indications that for the sodium halides some 25 to 75% of the beams consist of dimers. Miller and Kusch analysed the velocity distributions among the molecules effusing through an aperture from an isothermal enclosure for ten alkali halides. No dimerisation was found for caesium chloride or bromide, but appreciable concentrations were detected in the cases of lithium chloride and bromide, sodium fluoride, chloride and iodide, potassium chloride and iodide and rubidium chloride. Observable concentrations of trimers were found for lithium chloride and bromide for sodium fluoride. Values of ΔE° for the reaction $2MX = (MX)_2$ at temperatures around 850°K ranged from -42 to -48 Kcal.

The effects of dimerisation on the interpretation of the present results for lithium, sodium and potassium fluorides has been treated as follows. Values of the standard entropies of the gaseous dimers were estimated following the

assumption that they take up a planar configuration[25] with an apex angle of 105° and with bond-distance greater by 10% than in the monomer. Vibrational contributions to the entropy were estimated assuming five stiff modes with $\nu_2 = (r_1/r_2)^2 \nu_1$, (where subscripts $_1$ and $_2$ refer to monomer and dimer respectively) and one loose vibration with $\nu = 0.1\,\nu_2$. If a value of ΔH (dimerisation) is assumed, values of the equilibrium constant between monomer and dimer may be calculated, and hence partial pressures of the two species. The value of ΔH (dimerisation) may then be varied so as to bring the second and third law estimates of $\Delta_s H_{298}$ into agreement.

The results of these calculations are given in tables 2 and 3.

TABLE 2

Substance	temp. °K.	p_1, mm	p_2, mm.	$(\Delta_s H_T)_1$ kcal/mole	$(\Delta_s H_T)_2$	ΔE
LiF	1000	4.14×10^{-4}	3.28×10^{-4}	62.7	70.4	53
	1120	1.22×10^{-2}	1.57×10^{-2}			
NaF	1030	7.10×10^{-4}	0.45×10^{-4}	64.4	74.8	52
	1165	2.73×10^{-2}	0.38×10^{-2}			
KF	900	6.79×10^{-4}	0.45×10^{-4}	54.6$_5$	62.3	45
	1020	2.47×10^{-2}	0.31×10^{-2}			
KCl	830	4.88×10^{-4}	1.59×10^{-4}	51.0	54.1	49
	940	1.82×10^{-2}	0.74×10^{-2}			

TABLE 3

VALUES OF $\Delta_s H_{298}$ Kcal/mole

	(i) 100% monomer		(ii) corrected for dimerisation.		Best value
	second law	third law	second law	third law	
KCl	53.92	52.72	53.92	52.88	52.88
LiF	70.37	64.8	66.7	66.27	66.3
NaF	68.91	67.1	67.9	67.3_5	67.3_5
KF	58.97	57.6	58.1	57.77	57.8
RbF	55.63	54.83	-----	-----	54.9
CaF	48.72	49.12	-----	-----	49.1

Notes. 1. Miller and Kusch[7] find that for potassium chloride in the same temperature range as in our experiments, p_1 is about 91% of the total pressure, the third law value has been corrected accordingly.

2. If the second law values for rubidium and caesium fluorides are assumed to be correct, then we obtain $S^o_{(c)298} = 16.5$ and 19.6 cal deg^{-1} $mole^{-1}$ respectively, in fair agreement with Latimer's estimates[13] of 17.4 e.u. for rubidium fluoride and 19.1 e.u. for caesium fluoride.

The estimates of the extent of dimerisation are not to be regarded as more than semi-quantitative: they depend too strongly upon the second law values of the heats of sublimation for precise estimates to be made. For example, in the case of potassium chloride, Miller and Kusch find that the partial pressure of monomer is constant at about 91% of the total pressure in the temperature range 872 to 967°K. while the present work gives about 75%. However, since the heats of sublimation of monomer and dimer are so similar in this case, the method is very prone to errors in the experimental heat of sublimation by the second law. However, with this exception, the results are very reasonable. Dimerisation is of decreasing importance from lithium fluoride to potassium fluoride and has not been detected in rubidium or caesium fluorides. The values found for the energies of dimerisation, ranging from 53 to 45 Kcal $mole^{-1}$ fit well with those obtained for the other halides by Miller and Kusch. It seems that of all the alkali halides, lithium fluoride shows the greatest tendency to form dimers. Only in this case is the effect of dimerisation sufficient to change appreciably (by 1.5 Kcal), the value calculated from the third law on the assumption that the vapour consists solely of monomer.

The dissociation energies to ions of the alkali fluoride were calculated a) from a thermochemical cycle using the quantities given in circular 500 and the experimental heats of

sublimation, b) from Rittners theoretical model. The results are shown below and are compared with the spectroscopic values from Barrow and Caunt (1953).

TABLE 4

Heat of dissociation to ions.

	kcal/mole		
	Rittner	Thermochemical	Barrow and Caunt
LiF	177.8	175.1	-
NaF	155.3	150.5	-
KF	140.6	135.6	141.4
RbF	136.0	130.1	140.7
CsF	132.1	123.8	138.4

Appendix

Using plates of high resolution, taken on a 21ft. grating by Professor P. B. Zeeman of the University of Stellenbosch, the rotational analysis of the $^1\Sigma_g^+ - {}^1\Sigma_u^+$ (Mulliken) system of C_2 originally carried out by Landsverk[27] (1939) has been extended. The combination differences for the ground state found by Phillips[28] (1948) from the $^1\Sigma_g^+ - {}^1\Sigma_u^+$ system were combined with those from the present work to find accurate values of B and D for the lower state. It was hoped that perturbations of the singlet states by the triplet states might have made it possible to estimate the relative energies of the singlet and triplet states, but no evidence for perturbation was found.

The values of B_v, D_v and ν_o are given in Table 5 below.

Table 5

v'v''	o	B''	B'	D''x10^6	D'x10^6
0	43226.97	1.81171_3	1.82372_1	7.1475	7.4815
1	43201.17	1.7939_3	1.80493_7	7.190	7.518
2	43175.52	1.7757_8	1.7858_{96}	7.233	7.531
3	43150.86	1.7558_0	1.7651_9	7.50	7.67
4	43128.13	1.7380_5	1.7474_4	7.5	7.5
5	43108.86	1.719_9	1.729_{51}	7.5	7.5

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TABLE OF CONTENTS

LIST OF DIAGRAMS ETC.

LIST OF DIAGRAMS ETC. (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF TABLES (Continued)

GENERAL INTRODUCTION

In order to further the study of the nature of chemical bonding, it is essential to have accurate values of the dissociation energies of simple molecules. The three main methods of determining dissociation energies use spectroscopic, thermo-chemical and electron impact techniques. Recently the shock wave technique has also been used to find dissociation energies.

In ideal cases, the spectroscopic method provides an exact and unambiguous value, as for the halogen, O_2 and H_2 molecules, but in most cases, the dissociation limit is not directly observable and the Birge-Sponer or some other extrapolation must be used which may lead, as in the case of the K_2 molecule, to considerable error. A further drawback to the spectroscopic method is that it is necessary to know the states of excitation of the products of dissociation. Where these cannot be found from internal evidence, another value of the dissociation energy must be used in order to decide between the possible alternatives associated with the various possible energies of excitation.

In the thermo-chemical method the substance is taken through a series of reactions and physical changes which form

a thermo-chemical cycle. If one of these reactions is the dissociation of the gaseous molecule to atoms, and the heats of reaction for all the other steps in the cycle are known, the heat of dissociation is easily calculated. The disadvantage of this method is that the answer contains the sum of all the errors in the separate steps. However, this method is extremely valuable where the other methods fail. It is valuable for enabling a decision to be made between alternative spectroscopic values. It may also demonstrate the presence of maxima in the potential energy curves of molecules as for example in AlF.

In thermo-chemical cycles of this type, the least well known quantity is usually the heat of sublimation of the solid substance. The calculation of this requires accurate knowledge of the vapour pressure over a range of temperatures.

The alkali halides form a well defined class of substances which are amenable to theoretical treatment. Several theoretical treatments of the diatomic alkali halide molecule have appeared recently (Rittner (1952) Varshni (1957) Pauling (1956) Benson and Van derHoff (1954)) and the thermo-chemical data on the solid substances are now more complete. The spectroscopic method of finding the dissociation energy is not entirely satisfactory since the upper states are repulsive and only diffuse fluctuation bands are observed in the ultra

violet spectra. Interpretations of the spectra are prone to large systematic errors and the thermo-chemical method is preferable. For the alkali fluorides data on the vapour pressure over the solid are scanty. Data exist for the vapour pressure over the liquid, but the agreement between the work of the various authors is not very good. The heats of fusion mostly derive from measurements on the freezing points of binary mixtures, of doubtful accuracy; and the corrections to room temperature from the high experimental temperatures required for work on the liquids are large and uncertain. It seemed necessary therefore to measure the vapour pressure over the solid and so determine the heat of sublimation directly. A further point is that considerable evidence now exists for the presence of polymers in the vapours of the alkali-halides (Miller and Kusch (1956)) though there is controversy about this (Klemperer and Rice (1957), Rice and Klemperer (1957)), which, unless their concentrations were known, would interfere with the calculation of the heat of sublimation. The concentration of polymers in the vapour would be expected to increase with pressure, therefore it is preferable to make themeasurements at the lowest pressures possible.

It was decided to investigate the vapour pressure over the solid alkali fluorides, on which there is little data,

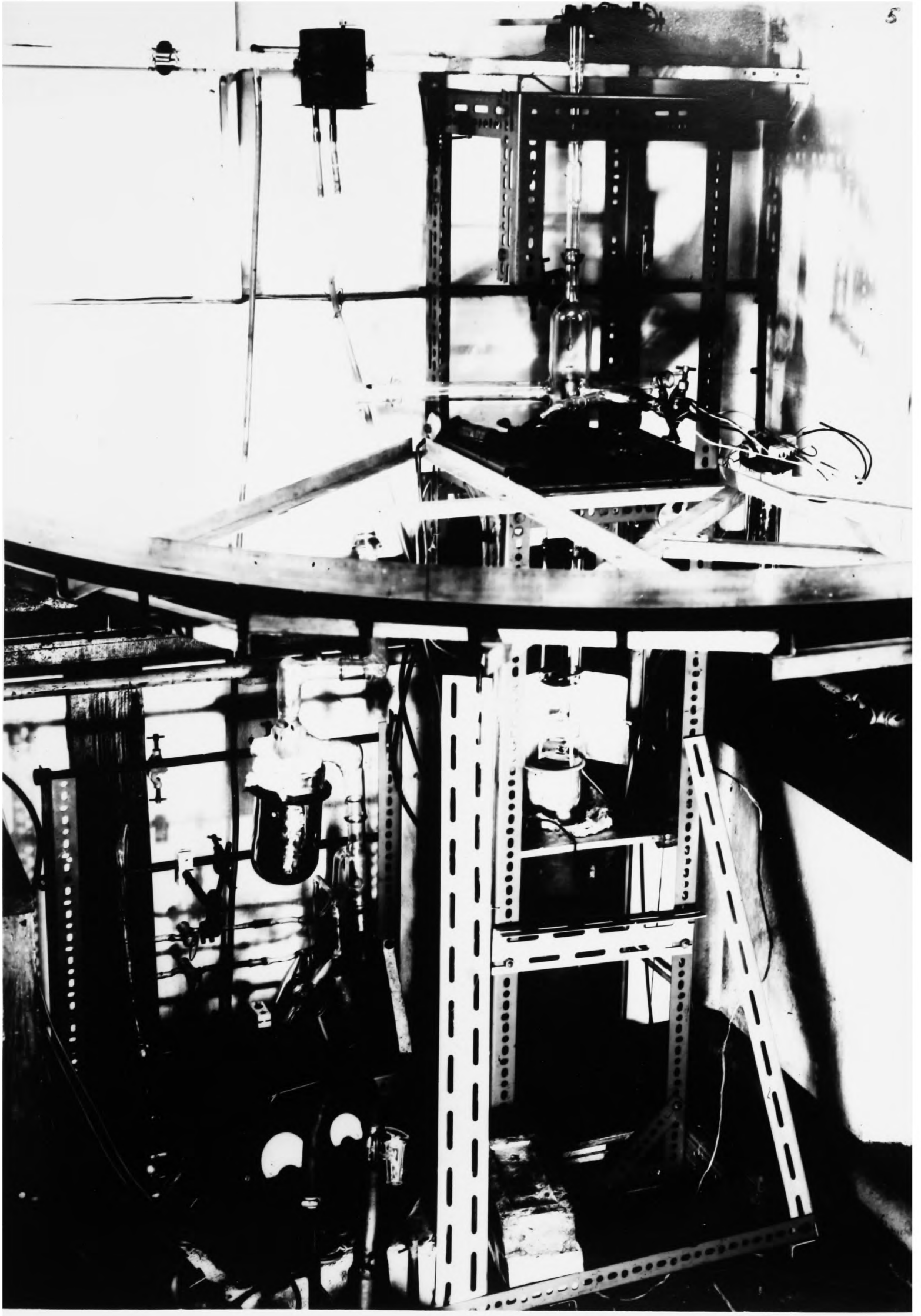
in order to obtain accurate values of the dissociation energies of the diatomic alkali fluorides as tests for the theoretical treatments: and also in the hope of providing evidence about the existence of polymers in the vapours of these substances.

This thesis is divided into three parts - the first deals with the construction of the apparatus, the second with the results obtained and in the third, the binding energies of the alkali fluorides, and the existence of polymers in the vapours are discussed.

In an appendix, an extension of the analysis of the system of C_2 originally carried out by Landsverk (1939) is described. It was hoped to find perturbations which would lead to a knowledge of the relative energies of the ground states of the singlet and triplet systems.

PART I

CONSTRUCTION AND CALIBRATION OF THE APPARATUS



Apparatus with furnace lowered

Fig. 1

INTRODUCTION

Since there are several excellent reviews of the general field of vapour pressure measurement, (Eucken (1935), Ditchburn and Gilmour (1941), Stull (1947), Dushman (1949), Speiser and Johnston (1950)) none will be attempted here. When intending to carry out vapour pressure measurements, it is necessary to decide whether a low ($< 10^{-1}$ mm) or a high pressure ($>$ 1 mm.) method is to be used. The reasons for the choice of the former for work in this laboratory have been given by Jeffries (1952). They are:

1) Observations are made at lower temperatures which are more easily obtained and measured.
2) The correction to be applied in converting the heat of sublimation at the experimental temperature to that at room temperature, will be smaller and errors due to the use of inaccurate thermal data will be correspondingly reduced.
3) It is often possible to make measurements on the solid. This removes the necessity for knowing the latent heat of fusion, which is seldom accurately known for inorganic compounds.
4) It is most commonly found that the vapour over a condensed phase contains a higher proportion of plymers as the temperature rises (Brewer 1950).

Heis (1924) described a method of measuring the vapour pressure of substances in the low pressure range in which the recoil force on the vessel due to molecules leaving it through a small hole was measured by the torsion in a fine quartz fibre. The method has been employed by Volmer (1931), Neumann and Volker (1932), Balson (1947) Wessel (1951) Searcy and Freeman (1954). The great advantage of the method over the usualweight-loss effusion techniques is its rapidity. The pressure is instantaneously measured, and a complete series of measurements over a wide pressure range is obtained in the time required for a very few points by the weight-loss method. Since the method gives the pressure directly without any assumptions concerning the molecular weight of the molecules in the vapour it can be combined with the Knudsen weight-loss effusion method to yield values of the molecular weight of the vapour. This application of the method has been used by Volmer (1931), Searcy & Freeman (1954) and Magee (1955). It was originally intended to measure molecular weights in the present apparatus, and a sensitive quartz micro-balance capable of carrying over 10 grams was constructed for this purpose, but so far, it has not been incorporated, and work has been restricted to the measurement of pressures only.

The torsion-effusion method has been used for the measurement of vapour pressures in this laboratory by

Jeffries (1952), Swinstead (1954), Pugh (1955) and Smith (1956). This apparatus has the furnace inside the vacuum envelope, which restricts the temperatures at which measurements can be made. For work on the alkali fluorides and other involatile substances, the construction of a high temperature version of the tension effusion apparatus was undertaken by the author.

DESCRIPTION OF THE APPARATUS

From experience in the use of the low temperature vapour pressure apparatus which has been in use in the department, the following improvements were incorporated in the present apparatus:

1) Loading from below so that suspension is not disturbed during re-loading;
2) Anti-vibration mounting;
3) A means of damping out oscillations of the suspension;
4) Increased length of scale;
5) External furnace.

Main frame-work

The main framework consists of four vertical lengths of Dexion slotted angle five feet in length, joined so that they form the corners of a square side 13" when viewed from above. Lengths of Dexion braced to the vertical members stick out from two adjacent bottom corners of the square and carry at their ends levelling feet. The main frame rests on four Lacrosse balls placed between pairs of 'Mascolite' fibre cups. The lower cups are supported on plywood supported on a further

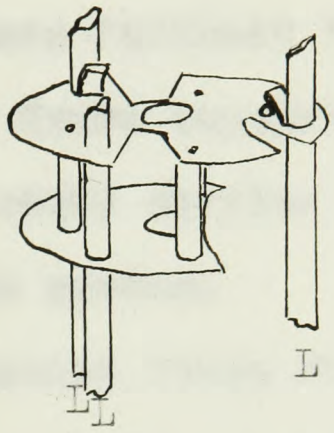
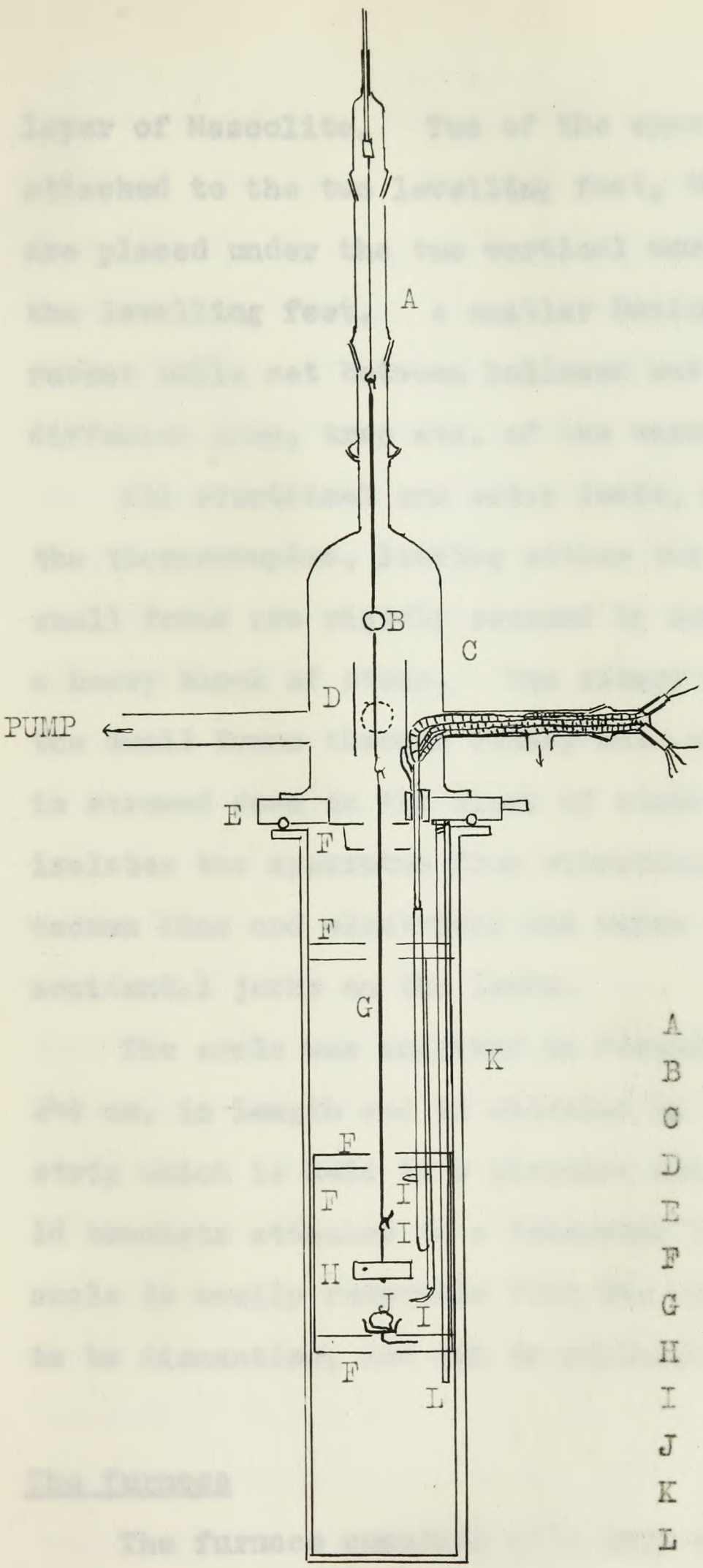


Fig. 2a



A	QUARTZ FIBRE
B	MIRRORS
C	DEWAR BLANK
D	COPPER CYLINDER
E	WATER-COOLED FLANGE
F	RADIATION SHIELDS
G	QUARTZ SUSPENSION ROD
H	EFFUSION VESSEL
I	THERMOCOUPLES
J	RADIOACTIVE SOURCE
K	SILICA POT
L	SUPPORTING RODS

Fig. 2

layer of Mascolite. Two of the upper fibre cups are attached to the two levelling feet, the remaining two are placed under the two vertical members furthest from the levelling feet. A smaller Dexion frame supported on rubber balls set between hollowed out corks carries the diffusion pump, trap etc. of the vacuum system.

All electrical and water leads, except those from the thermocouples, leaving either the main frame or the small frame are rigidly screwed by means of metal clips to a heavy block of stone. The rotary pump is connected to the small frame through rubber hose and a copper tube which is screwed down to the block of stone. This effectively isolates the apparatus from vibrations transmitted along the vacuum line and electrical and water leads, and from accidental jerks on the leads.

The scale was engraved on Perspex by hand. It is 240 cm. in length and is attached by brass screws to a steel strip which is held in a circular arc of 1 metre radius by 18 brackets attached to a framework of Dural angle. The scale is easily removable from the apparatus, when this has to be dismantled, and can be replaced exactly.

The furnace

The furnace consists of a coil of nichrome wire of resistance 0.404 ohms per yard wound with ten turns to the

inch on a spirally grooved silica former 20" long and 4" internal diameter. The coil is tapped at distances of 8 cm., 17 cm., 32 cm., and 41 cm. from the top edge of the former: the tappings are of nichrome and were spot welded to the coil. The coil is secured at each end of the former by a nickel band clamped round it by means of a stainless steel nut and bolt. The silica former is held in place between two square asbestos boards having 4" holes through the centre with a rabbet round the edge into which the former fits. The former is surrounded by a cylinder of mild steel sheet 9" in diameter which fits into circular grooves in the asbestos boards. Four iron rods threaded at each end pass through holes in the asbestos boards and force the steel cylinder into the grooves. The space between the former and the steel cylinder is filled with asbestos powder. The furnace leads and the tappings are insulated with porcelain beads and are fastened to terminals bolted to the top asbestos board. At each corner of the two asbestos boards a small piece of channel section girder is secured carrying at its end a small rubber-tyred Meccano wheel which fits into the corner of one of the vertical members of the main frame. The furnace can therefore be raised and lowered within the main frame and is retained in the centre of the frame by the small wheels. Lead counter

weights attached to wires running over pulleys facilitate this movement.

The envelope.

The envelope consists of two parts separated by a water cooled flange. The upper part is a pyrex Dewar blank selected for its optical quality since light incident upon and reflected by the galvanometer mirror on the suspension has to pass through it. It is flanged at its lower end and carries side arms for the main vacuum line, vacuum gauges and thermocouple leads. At its upper end it carries a female spherical ball grind. The male half of the ball grind is part of the tube containing the quartz fibre. The spherical ball joint makes it possible to adjust the suspension so that it hangs correctly along the axis of the lower part of the apparatus.

The lower part of the envelope consists of a silica tube 24" long 3" internal diameter closed at the bottom and having a 4" diameter ground flange at the top. The water cooled flange is of brass and is fitted with lugs by means of which it is rigidly bolted to the main frame. These lugs support the entire weight of the envelope. The top surface of the flange is flat and the pyrex flange is joined to it by vacuum grease. The lower surface has a circular groove cut in it into which is fitted $\frac{1}{8}$" diameter rubber cord

forming a type of "O" ring gasket. The flange of the silica pot is pressed against this gasket. The silica flange is not very smooth and it was found to be important that the length of rubber cord used was exactly right. If it was too short the ends were not forced together sufficiently strongly to prevent a leak, while if it was too long it became slightly bunched in the groove so that the silica flange was pressed less tightly against it in some places than in others. A great deal of time was spent looking for minute leaks which are now believed to have been due to this cause.

Radiation shields.

If we are to measure the temperature of a body in a vacuum by means of a thermocouple placed near it, the temperature measured will only be correct under "black body" conditions since it is extremely unlikely that the body and the thermocouple will have identical emissivities. Accordingly, an attempt was made to simulate as closely as possible a constant temperature enclosure using polished radiation shields.

Into the water cooled flange are screwed three metal rods which serve to support the radiation shields and thermocouples inside the silica pot.

There are three radiation shields all being constructed

on the principle of the 'light trap'. Each shield consists of two discs of molybdenum sheet, a short distance apart, with slots cut in them in such a way that gas can flow through them but the two discs together present a complete disc to incident radiation. A sketch of the radiation shields is given in Figure 2a. The discs are separated by short lengths of alumina capillary through which pass lengths of nichrome wire which are riveted at each end to join the shields to the spacer. Holes were drilled in each shield for the suspension to pass through, and other holes and slots for the thermocouples. Three more holes were drilled near the edge through which the metal supporting rods pass. The latter have narrow cuts made in them into which the edges of the corresponding holes in the radiation shields are forced by small copper wedges forced between the rod and the other side of the hole. The top radiation shield is just below the top of the furnace when this is raised to the operating position in order to blank off what would otherwise have been a "cold window." The next radiation shield is 20cm below the top of the furnace and the bottom shield is a further 15cm below this. The space between the two lower radiation shields forms the constant temperature enclosure and another radiation shield in the form of a cylinder of thin metal sheet stretching between the two circular radiation shields completes the enclosure. All

radiation shields were polished and retained this polish on heating since the metal oxides were volatile at the experimental temperatures. A discussion of the metals used for supporting rods and the cylindrical radiation shield is given later.

The vacuum system.

The vacuum system is entirely conventional. It consists of a Metrovac Type 02 oil diffusion pump backed by a two stage Metrovac rotary pump, a cold trap surrounded by liquid air freezes out condensible vapours. Large diameter tubing was used in order to obtain a high pumping speed. A system of two ground glass spherical joints and a cone and socket joint make possible considerable relative movement between the main apparatus and the vacuum system mounted on its separate frame. After out gassing, vacua approaching 10^{-6}mm were often obtained.

The residual pressure in the apparatus was measured by a thermocouple gauge and an ionisation gauge.

The cooling water flowing through the water cooled flange and the diffusion pump was fed to a constant head tank with a capillary leak at the bottom. A float-operated micro-switch switched off the diffusion pump and sounded a warning buzzer if the flow of water became less than that passed by the capillary leak. An Edwards type VSK.1 vacuum

relay was incorporated which switched off both the diffusion and rotary pumps if the pressure in the system rose above 2cm.

The suspension.

The suspension consists of three parts: the quartz fibre, a pyrex rod bearing the mirrors, a silica rod to which the effusion vessel is hooked.

The quartz fibre was made by the following method. A hook was formed on the end of a short length of 1mm quartz rod; the other end was waxed into a piece of pyrex capillary joined to a length of 4mm pyrex rod which was clamped vertically. From the hook was suspended a piece of glass rod weighing a few grams. The glass rod was surrounded by a piece of 12mm pyrex tubing clamped vertically. In order to draw out a fibre, a very small silent coal gas-oxygen flame was applied to the centre of the quartz rod until the weight began to fall, when the flame was quickly removed. The height which the weight can fall before striking the bench determines the length of the fibre. The fibres used were about 25cm long. When the weight falls it must not be checked by touching the walls of the glass tube. It usually took many attempts before a fibre of the correct length and torsional constant was obtained.

Measurement of Deflection.

The second section of the suspension is a thin pyrex

rod carrying two concave galvanometer mirrors of 1m. focal length, and a radiation shield. The mirrors reflect light from a galvanaometer lamp on to the circular scale. In this way the deflection of the suspension from the zero position is measured. The two mirrors are joined back to back to the pyrex rod with shellac cement. By using two mirrors, a second set of observations (hereinafter called '<u>high points</u>') when the suspension has made half a revolution can be obtained. The angle between the mirrors was found by the following method.

Two galvanometer lamps with their lenses half masked and having thick vertical cross-wires fixed to the surfaces of them, were placed two metres apart. They were adjusted so that the image of the cross-wire of one lamp coincided with the cross-wire of the other. A horizontal translucent scale was placed level with the lens of one lamp at right angles to the line joining the two lamps. The mirror system was placed one metre from the lens of the lamp having the scale near it, so that it interrupted the beam of light. The mirror system was turned until the image of the cross-wire of the lamp not having the scale near it was reflected back upon the cross-wire. The image of the cross-wire of the other lamp was reflected on to the horizontal scale and its distance from the cross-wire was recorded. This distance in cm when corrected for the fact that the translucent scale

was not the arc of a circle of 1 metre radius is the quantity which must be added or subtracted to the readings of deflection during a high point measurement. Below the pair of mirrors, a small aluminium radiation shield is retained between two bulges in the pyrex rod. Its purpose is to protect the mirrors and fibre from the effects of radiation.

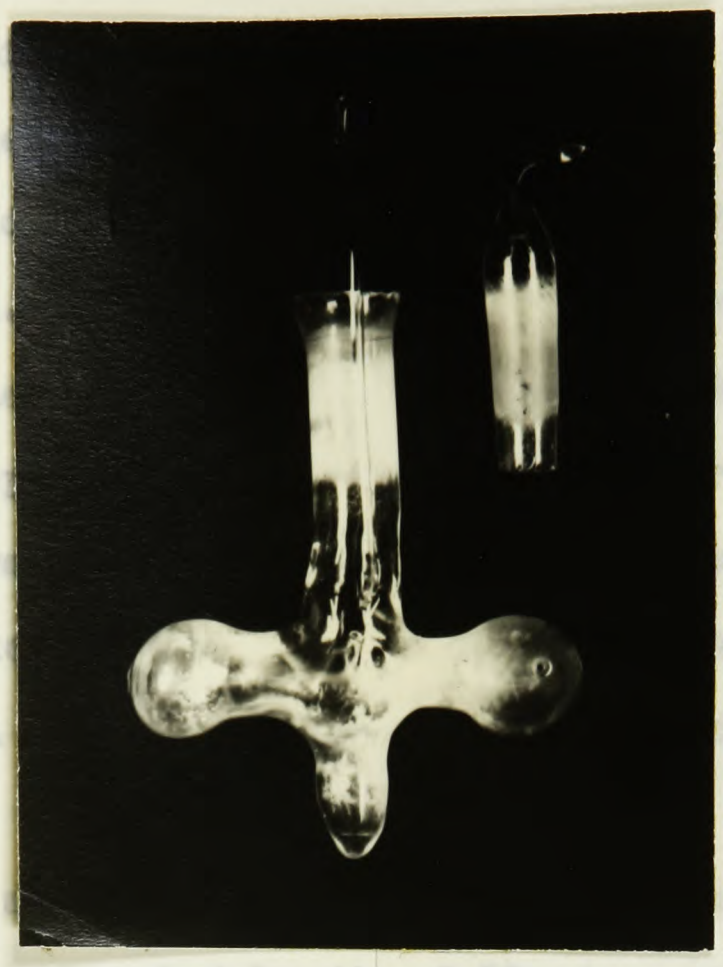
The remainder of the suspension consists of a thin quartz rod with hooks at each end carrying the effusion vessel at one end and attached to the pyrex rod at the other.

All hooks were made acute to obviate angular movement between two hooks; the centre of each hook lay on the axis of the rod.

The effusion vessels.

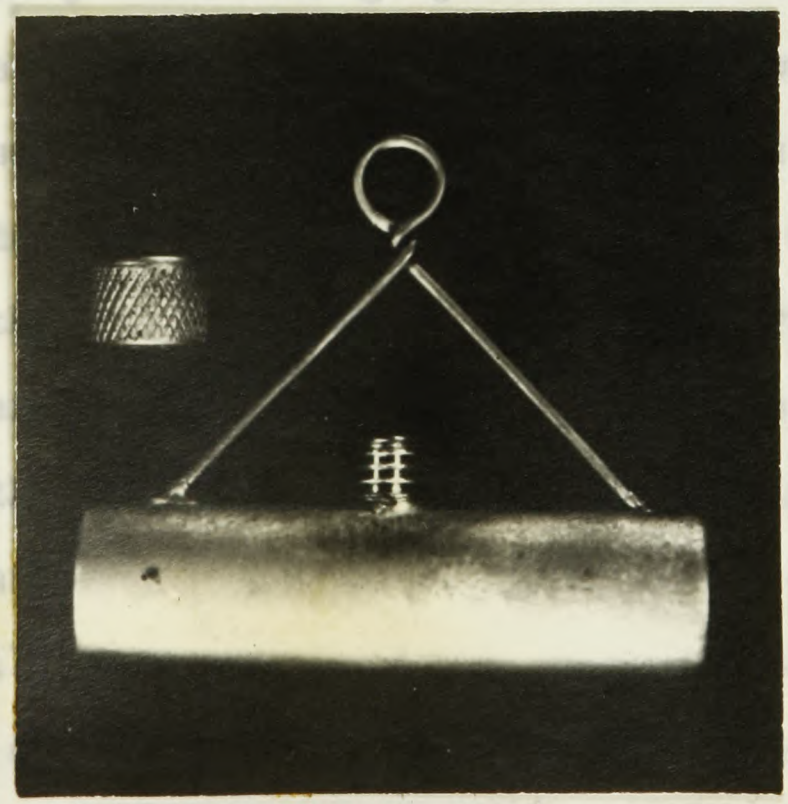
Effusion vessels made from the following materials were tried: quartz, graphite, alumina, copper and platinum. These will be described separately.

The quartz vessel is illustrated in Figure 3. It was made by the usual techniques of silica blowing using an oxygen-coal gas flame. First of all the bulbs were blown and joined to a piece of tubing closed at one end. The holes were then made using the technique given by Weselovskii. A very small flame was played on the surface of the bulb, and a small hole was blown. By playing the flame on the hole it can be made to shrink and finally to disappear. At the same



QUARTZ VESSEL

Fig. 3



PLATINUM VESSEL

Fig. 6

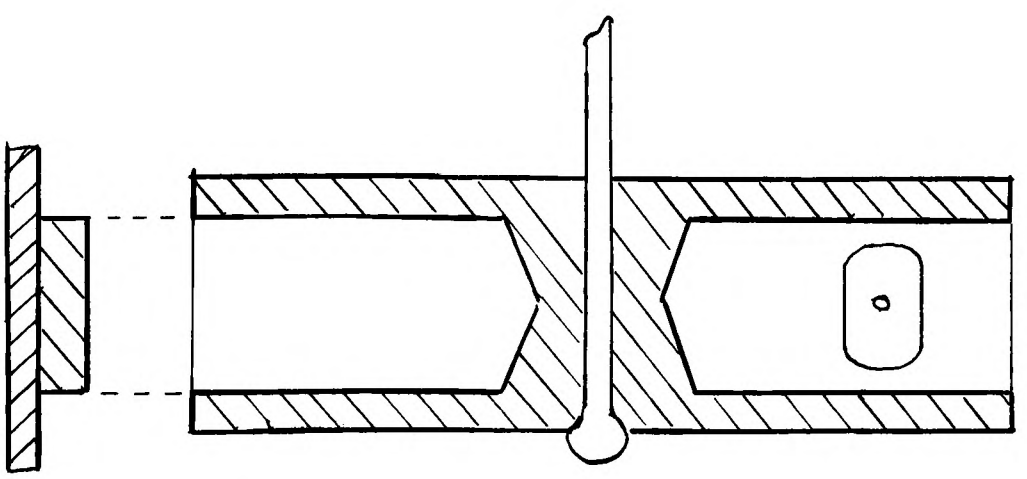
time the wall of the bulb tends to collapse but by combining shrinking of the hole with an occasional blow which blows out the bulb and also enlarges the hole, a satisfactory hole can be obtained. The holes so produced have wall thicknesses much thinner than the general thickness of the surrounding bulb. No attempt was made to reduce further the wall thickness since it was thought that the thin edges of the hole might be attacked by the alkali halide vapours. The vessel was closed by a ground stopper, and a suspension hook was added.

Quartz is attacked by the alkali fluorides so graphite vessels were constructed by the following method. A photograph of a graphite cell is given in Figure 4 and a scale drawing in Figure 5 .

A length of $\frac{5}{8}$" diameter graphite rod (obtained from Morgan Crucible Co. Described as Link EY 9a) was first turned down to $\frac{1}{2}$" diameter in the lathe. The end was turned flat and a hole $\frac{5}{8}$" deep was drilled along its axis using a 11/32" drill held in the tail stock. The rod was parted off about $1\frac{3}{4}$" from the turned face. The small piece was then mounted in the chuck, the face was then turned down flat until the total length was $1\frac{3}{8}$". Another hole 11/32" in diameter and $\frac{5}{8}$" deep was drilled along the axis. This left a solid section $\frac{3}{8}$" long in the centre of the vessel. Since it was found that the drill did not always give a perfectly round parallel

GRAPHITE VESSEL

Fig. 4



GRAPHITE VESSEL SCALE 1:2 : 1

Fig. 5a

sided hole, the holes were very slightly enlarged for a distance of about $\frac{1}{8}$" from the end of the vessel, using an inside turning tool, in order to ensure that over this distance the walls of the hole form a perfect cylinder. Into these parts are fitted the gas tight plugs. Two small plugs were made by turning down the $\frac{3}{8}$" diameter graphite rod, which were a very tight push fit into the ends of the vessel. The length of plug which fitted into the vessel was about 1/10".

Three holes were next drilled in the vessel - the two effusion holes, and a hole 1/16" in diameter which passed through the centre of the vessel at right angles to the principal axis through which was to pass a quartz suspension rod. The holes were drilled using a simple jig. This consisted of a piece of copper tube $1\frac{5}{8}$" long and internal diameter $\frac{1}{2}$" with a 3/32" hole through its centre and two 1/16" holes in a direction at right angles to the centre hole $\frac{1}{4}$" from each end. These holes were drilled on a milling machine using the dividing head to ensure that they were at right angles to each other. The jig was mounted in a machine vice on the table of a vertical power drill so that a 1/16" drill could pass freely through the centre holes without touching the jig. The vessel was then placed in the jig and the drill again passed through the centre holes of the jig, drilling a hole exactly through the centre of the vessel. Keeping the vessel in the jig with the 1/16" drill stuck

through the centre hole to locate the vessel in the jig, the effusion holes were drilled. The jig was clamped in the machine vice for convenience and the effusion holes were drilled on opposite sides of the vessel through the 1/16" holes in the jig using a 1/64" drill clamped in a pin vice. The pin vice was held vertical by one finger resting on its end, while it was turned gently with the fingers of the other hand. This hole was then enlarged with a No.73 drill to give a hole about 0.6mm in diameter, using very light pressure on the pin vice to avoid breaking away the bottom of the hole when the drill went through. The area round the hole was then carefully filed away until the thickness of the hole was less than its diameter. The centre hole was elongated into a small slot at one end; a piece of silica rod 1/16" in diameter with a hook at one end was passed through the centre hole with the hook away from the slot. The end of the silica rod was heated until it was molten and then squeezed by a pair of pliers to form a thickish disc on the end of the rod which fitted into the slot at the end of the centre hole and prevented the vessel rotating about the silica rod.

Precautions were taken at every stage to avoid contamination by ferrous material. The lathe, lathe tools and drills were carefully cleaned before use and the pieces of graphite rod were wrapped in tin foil before being clamped in the chuck.

Due to snags which will be described later graphite was not found to be satisfactory as a cell material and a copper effusion vessel was made from a piece of $\frac{3}{8}$" diameter copper tubing which was drilled out to make the walls thinner except at one end which was left at the original thickness for a distance of 2mm. Plugs were made for each end. One was permanent, the other, at the end with the thick walls was removeable for loading the vessel. The vessel was not satisfactory since at the temperatures of the experiment ($900^{o}C$) the plugs were welded to the tube and were difficult to remove. Also the empty vessel gave off vapour which was probably carbon monoxide since the copper used was of industrial quality, not electrolytic. Copper effusion vessels should be useful at lower temperatures if they are made of electrolytic material.

Another vessel was made by boring two holes in a piece of recrystallised aluminia thermocouple sheath. The sheath was cut using a diamond saw and the wall thickness was reduced where the effusion holes were to be, also using a diamond saw. One hole was drilled using a sharpened tungsten point mounted in an electric drill with carborundum powder and water applied to the drill point. The other was drilled by discharging a large bank of high voltage accumulators used for a Lyman source between two electrodes placed either side of the tube wall. The ends of the cell were blocked by

aluminia cement. This was not satisfactory because of the low grade of cement used, but given better cement, the method should be satisfactory. Experiments showed that it is possible to make ground joints in aluminia. The socket was made by rotating the tapering part of a coarse rat-tail file dipped in a paste of coarse carborundum powder and water inside the end of the tube until it was sufficiently large to allow the plug to be pushed in and grinding was continued in the usual manner for glass and silica joints. The plug was tapered slightly on the diamond wheel before starting the grinding operations. It seemed to be possible to make an alumina effusion vessel using the closed end of a thermocouple sheath and a length of aluminia rod to form the plug, but experiments had to be discontinued due to shortage of materials.

Finally a platinum effusion vessel was made by Messrs. Johnson Matthey. It is 4cm long and weighs 13.9gr and has given satisfactory results.

The control and measurement of temperature.

In order to obtain as far as possible uniform temperature along the axis of the furnace the tappings along its length were shunted by rheostats so that extra current could be fed to the ends of the furnace which would normally be colder than the centre. In order to test the temperature distribution,

a silica tube, 5mm external diameter closed at the bottom was waxed into the position normally occupied by the fibre section of the envelope. The tube extended nearly to the bottom of the silica pot and the temperature at any point in the tube could be investigated by a chromel-alumel thermocouple threaded through twin bore silica which could slide up and down inside the tube. The temperature distribution was investigated at intervals of 25°C from 400°C to 850°C. At each temperature, the rheostats were varied to get the most constant temperature within the constant temperature enclosure. The greatest temperature gradient during vapour pressure measurements was 0.3°C per cm. Preliminary investigations of the temperature distribution without the radiation shields forming the constant temperature enclosure were carried out in order to decide the best position for these.

The current through the furnace and its shunts is controlled by a variac rated at 8 amps. A current of 6.5 amps was needed to maintain a temperature of 890°C. A system of switches enables one to find the current in any shunt or the total current through furnace and shunts using one ammeter. It was found possible to hold the temperature steady for long periods by manual control.

Daane (1950) during his work on the vapour pressures of silver and copper found that the calibration of the platinum-13% platinum-rhodium thermocouple is very liable to

be upset by contamination. He found that such a thermocouple even though protected by both aluminia and metal sheaths changed its calibration by 130°C after only a few hours working. He found that the chromel p-alumel thermocouple changed by only 4°C after over a week of continuous use. Accordingly a chromel p-alumel thermocouple was used in the present work. This type of thermocouple has the further advantage of a high rate of change of e.m.f. with temperature compared with the rare metal thermocouple.

Three thermocouples are used in the apparatus. The main thermocouple is sheathed with an aluminia sheath which has slots cut in the sides so that it is supported in slots cut in the radiation shields. The thermocouple is threaded through twin bore silica which reaches to the level of the water cooled flange. Thereafter until the waxed joint by which the wires leave the apparatus they are insulated by small ceramic beads. The other two thermocouples are unsheathed and are positioned one at each end of the constant temperature enclosure in order to check on the temperature distribution. Where the thermocouple leads bend over before entering the side arm by which they leave the apparatus, a copper cylinder mounted on the water cooled flange prevents them from touching the suspension.

The cold junctions were kept at 0°C in ice and water. They consisted for each thermocouple of a chromel-copper

junction and a p-alumel-copper junction so that copper leads to the potentiometer could be used without having any metal-metal boundaries in the thermocouple circuits at variable temperatures. The e.m.f's of the thermocouples were measured by a Tinsley potentiometer which was sensitive to .01mv which is equivalent to 0.25°C. The main thermocouple was calibrated at the freezing points of silver, aluminium and zinc. All the samples, of the highest purity, were contained in graphite crucibles with graphite lids through the centre holes of which passed recrystallised aluminia sheaths. The crucibles were placed in a tubular electric furnace mounted vertically and packed round with asbestos wool.

Two thermocouples were calibrated. With the first, the runs on the graphite cell were carried out, and with the second, those on the platinum cell. The calibration points are given below.

Freezing point of		E.m.f. thermocouple 1	thermocouple 2
Silver	960.5°C	39.49 m.u	39.47
Aluminium	660.0°C	27.42 m.u	27.45 m.u
Zinc	419.5°C	17.31 m.u	17.29

Roeser Dahl and Gowans (1935) have calibrated a chromel-p-alumel thermocouple over a wide range. Their results for the silver and aluminium points were plotted on a graph of e.m.f. against temperature and a straight line drawn through them. The deviations of their other points

Correction to be ADDED to the value of the temperature calculated from the equation.

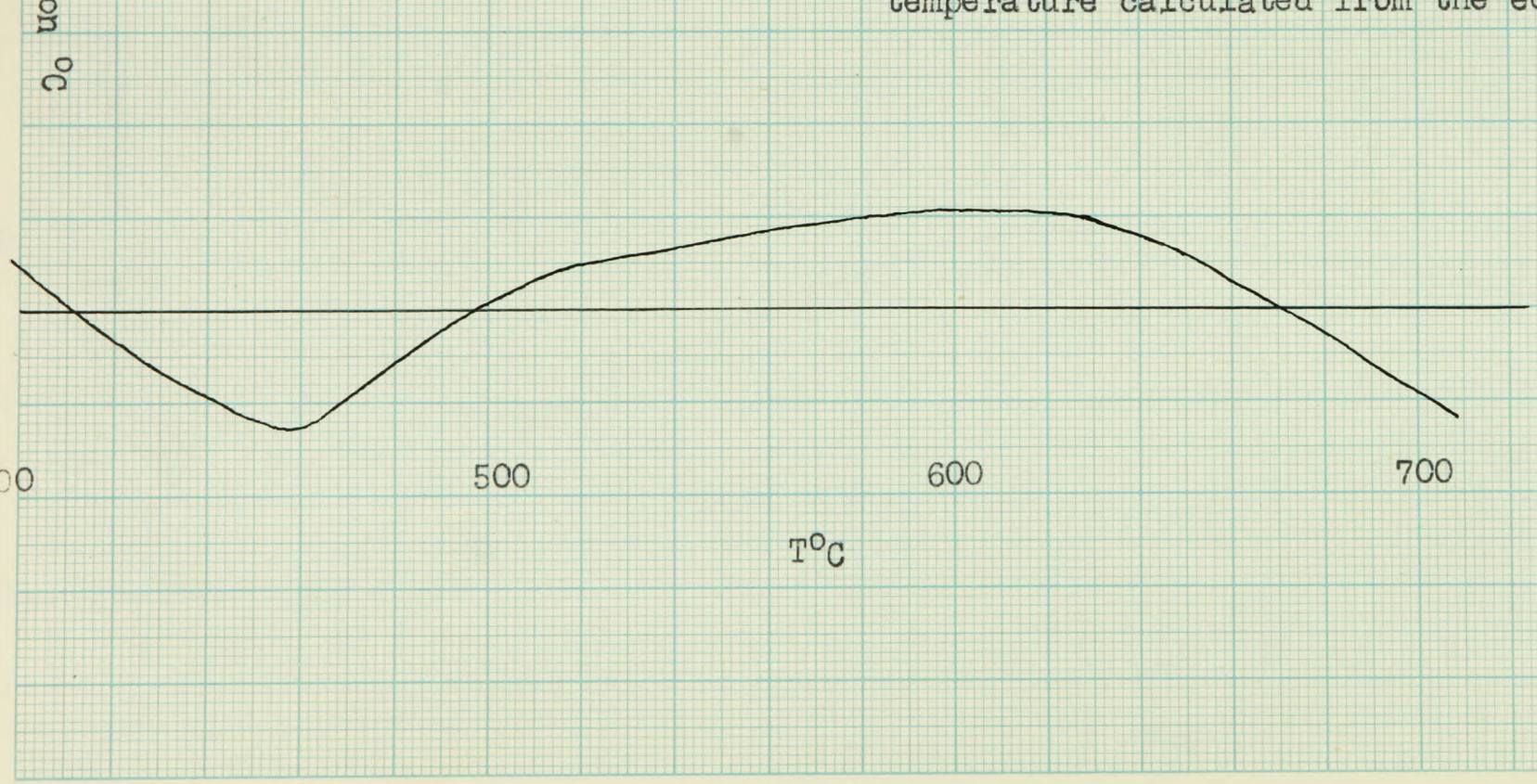


Fig. 7.

Correction to be ADDED to the value of the temperature calculated from the equation.

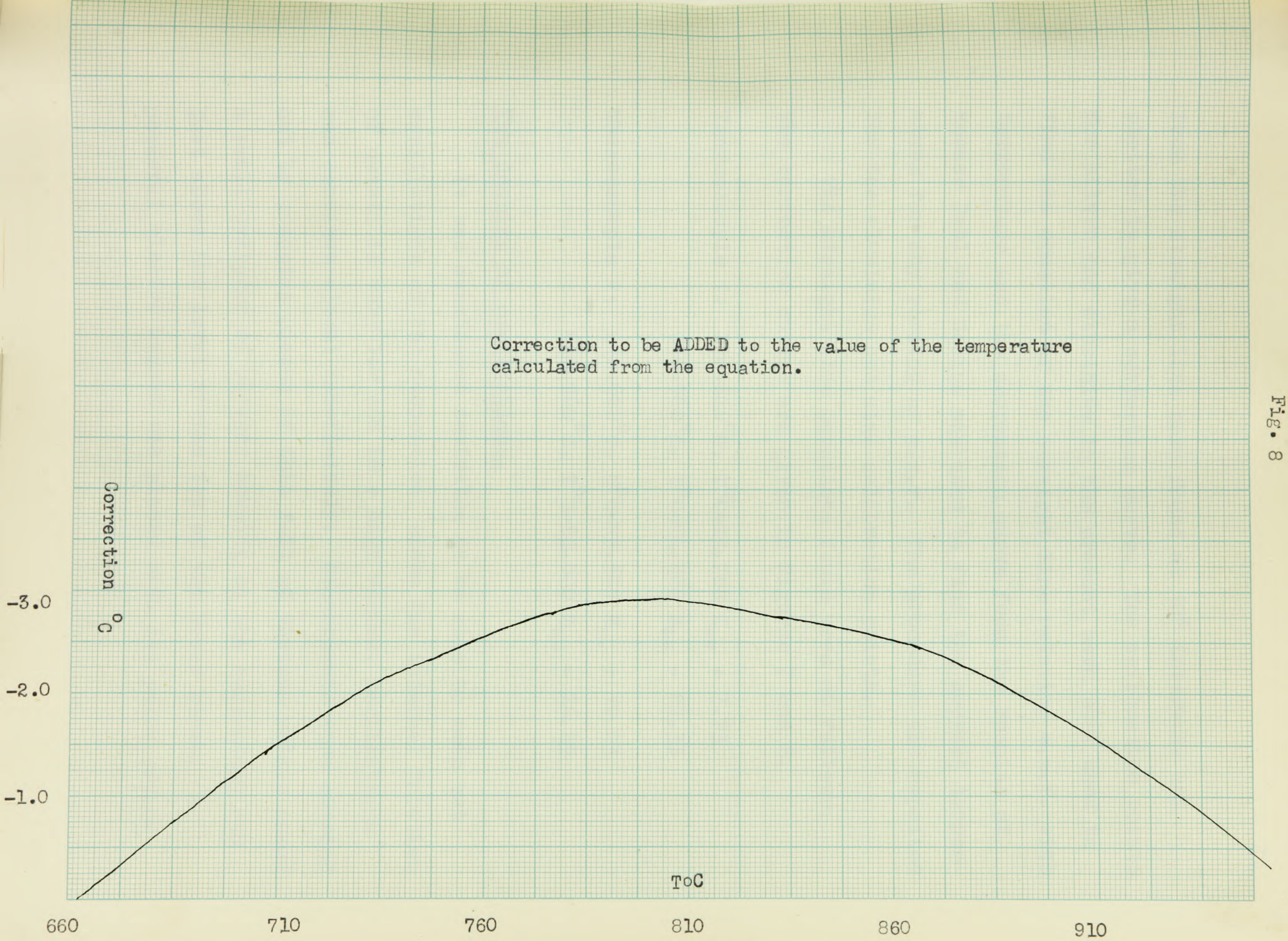


Fig. 8

from the straight line were found at 10° intervals and plotted to give a correction curve. The calibration points for silver and aluminium in the present work were used to find the equation of the straight line relating e.m.f. with temperature and the correction curve from the results of Roeser Dahl and Gowans was used to find the correct temperature for any reading of e.m.f. The procedure was repeated for the aluminium and zinc calibration points.

The straight line equations found were as follows. The correction curves are given in Figures 7 and 8.

Thermocouple 1: 420-660°C, $T^{\circ}C = 23.788\ E_{mV} + 7.73$

660-960°C, $T^{\circ}C = 24.888\ E_{mV} - 22.33$

Thermocouple 2: 420-660°C, $T^{\circ}C = 23.671\ E_{mV} + 10.23$

660-960°C, $T^{\circ}C = 25.000\ E_{mV} - 26.25$

The damping of oscillations.

It was considered desirable to be able to damp out oscillations of the suspension, since the internal friction of quartz is very low and in a high vacuum, oscillations can continue almost indefinitely. Experiments were carried out by wrapping pieces of thin foil of various metals round a small cylinder of perspex mounted on the suspension rod just above the level of the top of the Dewar blank. A powerful electro magnet was placed with its poles either

side of the tube leading to the hemispherical grind so that the metal cylinder turned in its field and eddy currents in the metal produced damping. Difficulty was experienced in finding metals sufficiently free from ferro magnetic impurities to prevent a deflection when the magnet was switched on. Silver was eventually used. It was found in practice, however, that although the damping was effective, the zero position of the system was very far from reproducible and eventually the cause was found to be electrostatic charges on the metal cylinder, so this method had to be abandoned.

During checking of the suspension for magnetic impurities, it was discovered that the mirrors were strongly magnetic and reacted to a horse shoe magnet held outside the envelope. This provided a method of damping which was effectively used. Experiments were carried out to discover if the earth's magnetic field or that due to the furnace exerts an appreciable force on the mirrors, but no such effects were found.

Experimental procedure.

The vessel was first loaded with the substance under test. A small glass funnel was used with the quartz and platinum vessels. For deliquescent substances being tested in the platinum vessel, the vessel was heated in a gas flame before being placed in the apparatus. The vessel was hung from the hook of the silica suspension rod, the radiation shields were put in place, the silica pot was raised to the

water cooled flange and secured in place by a metal clip, and the rotary pump was switched on. The furnace was raised to the operating position and the gap between the furnace tube and the silica pot was filled with asbestos wool. When the pressure had fallen to the lowest value attainable by the rotary pump, the diffusion pump was switched on. Meanwhile the oscillations of the suspension were damped out using the magnet. When the diffusion pump was working properly leaks were tested for by turning off the tap to the rotary pump and allowing the diffusion pump to pump into the small volume formed by the tubes of the high pressure side of the system. If after ten minutes there was no trace of nitrogen in the discharge excited by a Tesla coil in the high pressure side of the system, and no increase in the pressure on the low pressure side recorded by the thermocouple gauge, the tap to the rotary pump was reopened and out gassing was begun. This consisted of raising the temperature to a value higher than that which would occur during a run. This procedure drives off adsorbed gases both in the sample and on the rough walls of the silica pot. In practice the apparatus was heated until the suspension had made one complete revolution which was about 25°C higher than the highest temperature measured during a run. It was held at this temperature for about half an hour and then the current was switched off and the apparatus allowed to cool.

The following day, the zero position of the suspension was recorded. The suspension swung over a small arc of about 0.05 - 0.1 radians and the extreme positions of the spot of light were noted. The furnace was switched on and the rheostats adjusted to give the best temperature distribution for the highest temperature expected during the run. The spot of light moved off the scale when the temperature had risen sufficiently; the current was then cut down from the maximum and the heating was carefully controlled until the spot of light reflected from the other mirror reappeared on the zero end of the scale and eventually moved off the other end. This condition, with the spot just off the scale was maintained for at least $1\frac{1}{2}$ hours in order to allow the temperature distribution to settle down. The current was then reduced slightly so that the temperature began to fall very slowly at a rate not exceeding $1^{\circ}C$ in six minutes. The oscillations of the system were damped out by use of the magnet, if necessary, and when the spot of light reappeared on the scale, readings were taken at the extremities of the swing. At the same time, the temperatures shown by the three thermocouples, the time, and the residual pressure shown by the ionisation gauge were recorded. Readings were taken at intervals of about $2.5^{\circ}C$ until the spot moved off the scale. These readings taken when the suspension has turned through half a revolution and the spot of light is

reflected by the mirror other than that which reflects the spot during the zero readings, will be termed "high points."

The current was then slightly reduced and it was necessary to wait until the spot of light reappeared on the scale when the above procedure was repeated exactly except that readings were taken less frequently, until the deflection was about 20 cm from the zero.

Preliminary Experiments.

A large number of runs were carried out before satisfactory results were obtained. In order to prevent a repetition by future workers of these mistakes, a short account of them will be given.

Initially, the supporting rods within the furnace were of high temperature stainless steel. It was found impossible to obtain a good vacuum with these since carbon monoxide continued to be given off in large quantities even after prolonged heating in vacuum. Furthermore, a black deposit of a compound of iron (probably ferrous oxide which is quite volatile) accumulated on the cooler parts of the apparatus. The graphite effusion vessel became strongly magnetic presumably by reduction of ferrous oxide on its surface and was acted upon by the magnetic field in the furnace. Stainless steel is also unsatisfactory since manganese can distil out of it.

It was then decided to try to dispense with the lower radiation shields altogether and to retain only the shield level with the top of the furnace. Good vacua were obtained and the graphite vessel remained free from magnetic impurities, but it was found to be impossible to obtain consistent results. Both the absolute pressure recorded at a given temperature and the slope of the log (deflection) against $^1/T$ plots varied considerably from run to run.

The stainless steel rods were then replaced by nickel, with a cylindrical nickel radiation shield and the molybdenum radiation shields forming the constant temperature enclosure. Good vacua were obtained, but after a time the vessel again became contaminated by magnetic impurities.

Finally, copper rods were used with a cylindrical copper radiation shield and the molybdenum shields to form the constant temperature enclosure. After some heating good vacua were obtained. The volatility of copper is greater than of nickel and all objects within the constant temperature enclosure became copper plated. However, according to Daane (1950) the vapour pressure of copper at the highest temperatures used is only 4×10^{-6}mm. The vessel remained free from magnetic contaminants.

The graphite cell, despite promising results on potassium chloride did not in the end give satisfactory results. The greatest difficulty was the non-reproducibility of the zero

position of the suspended system, hereafter referred to as "the zero." Only for potassium chloride, for which a high point was also taken, were the results reproducible and this must be considered fortuitous. For sodium fluoride in particular, for one set of runs it was found impossible to obtain the zero when the apparatus was cold. Instead of returning to the zero position, it was frequently found that the suspended system was showing a negative deflection of from 10 to 60 cms. This was noticeable to a lesser degree for the more volatile substances, though usually by the following morning the system had returned to approximately the correct zero. In the end, for sodium fluoride, it was found necessary never to allow the furnace to cool down below about 500°C at which temperature sodium fluoride has a negligible vapour pressure. The zeros for these runs were reproducible and the runs themselves were in good agreement. For caesium fluoride it was not found possible to obtain even plausible results. High points were taken, but these lay considerably off the line through the low temperature points.

All the plots of log D against $^1/T$ obtained with the graphite vessel showed a slight curvature the gradient being steeper towards lower temperatures. This curvature was very marked for lithium and caesium fluorides. A detailed explanation for the unsatisfactory behaviour of graphite as

a cell material is not offered, but it is suggested that it is due to the adsorbtive properties of the material, especially when under the conditions of the experiment it has become 'active'. The low values for the heats of sublimation of the substances tested with the graphite cell suggest that adsorbed gases are still being given off in minute quantities at the low temperature end of the run, but nevertheless in sufficient quantities to form an appreciable fraction of the total gas pressure inside the cell and so lower the observed value of the heat of sublimation. If this were the case one would have expected the Log D against $^{1}/T$ graphs to be curved in the opposite direction. The zero was found to be quite strongly dependent upon the residual pressure, and it was noticed that a slight leak in the apparatus, even though the residual pressure might still be of the order of 2 or 3 x 10^{-4}mm was immediately reflected in the behaviour of the graphite cell. Deflections, in this case, became noticeably larger for points at the low temperature end of the run and smaller for points at the higher temperature end. The negative deflections observed when the apparatus was cold after the sodium fluoride runs suggest that the graphite was readsorbing gas through the effusion holes. However, the measured residual pressure was often of the order of 5 x 10^{-6}mm which would produce only a minute deflection. When the apparatus was allowed to cool

down after it had been kept above 500°C for four days and nights, a very large negative deflection occurred.

In view of these setbacks, and the unpromising results obtained with copper and aluminia effusion cells, it was decided to obtain a platinum cell. Lack of reproducibility of the zero was found also to be due to electrostatic charges being built up on the vessel. This trouble was cured by placing a small radio active source, formed by irradiation of the rock during the "Emu" atomic explosion, on the lowest radiation shield directly under the effusion vessel.

THERMODYNAMIC RELATIONS AND TREATMENT OF OBSERVATIONS

It will be convenient here to outline the thermodynamic relations used in this work.

There are two approaches by which the heat of sublimation may be calculated.

1) Second low treatment.

The heat of sublimation or vapourisation (ΔH) at a temperature $T^{o}K$ is given by the Clausius-Clapeyron equation

$$\frac{d \log p}{dT} = \frac{\Delta H}{2.3025\ RT^2} \qquad (1)$$

which an integration gives

$$\log p = \frac{-\Delta H}{2.3025\ RT} + I \qquad (2)$$

p is the pressure of vapour in equilibrium with the condensed phase and I is an integration constant.

The heat of sublimation or vaporisation at the temperature T is therefore obtainable from the tangent to the graph of log p against $^{1}/T$. In order to find the value of the heat of sublimation at room temperature from a series of experimental points, the method of Kelley (1935) was used.

If the difference between the specific heats of the gas and condensed phase is given by

$$\Delta c_p = \Delta a + \Delta bT - \Delta cT^{-2} \qquad (3)$$

integration gives the heat of sublimation or vapourisation at temperature T

$$\Delta H_T = \Delta H'_o + \Delta aT + \frac{\Delta bT^2}{2} + \Delta cT^{-1} \qquad (4)$$

where $\Delta H'_o$ is an integration constant.

If this value for ΔH is substituted in equation (1) integration gives

$$-R\ln p + \Delta a \ln T + \tfrac{1}{2}\Delta bT - \tfrac{1}{2}\Delta cT^{-2} = \Delta H'_{o/T} + I \qquad (5)$$

the left hand side of this equation is denoted by the symbol Σ

The value of Σ was found for each experimental point and the slope of the graph of Σ against $^1/T$ was found by the method of least squares. The value of I was found for each point and bad points were rejected. The new value of the slope was found and the constant $\Delta H'_o$ calculated. The standard deviation and 95% confidence limit were found for each run. The best values of $\Delta H'_o$ and I for each substance were found by weighting the values obtained from the various sets of observations according to the inverse squares of their standard deviations.

The differences of the several values from the weighted mean were used to find the standard deviation of the mean and thence the 95% confidence limits of the mean.

For data on the solid, the heat of sublimation at room temperature was found by substituting the value 298.16°K for T and the weighted mean value of $\Delta H'_o$ in equation (4).

For data on the liquid, the heat of vapourisation at the

melting point was found first by substituting the value of the melting point in equation (4); adding to it the heat of fusion gave the heat of sublimation at the melting point. Using this value in equation (4) and the values of Δa, Δb and Δc for the solid-gas equilibrium, $\Delta H_o'$ for the sublimation of the solid was found, and hence the heat of sublimation at 298°K as above.

2) Third law treatment.

For the equilibrium

$$\text{Condensed phase} \rightleftharpoons \text{gas}$$

the free energy change must be zero.

At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S = 0 \qquad (6)$$

$$H = T\Delta S \qquad (7)$$

where ΔH is the difference between the heat contents of the gas and the condensed phase, and ΔS is the difference in their entropies. If therefore we have sufficient data to calculate the entropies of gas and condensed phase at the temperature T we can calculate the heat of sublimation or vapourisation at this temperature, and from a knowledge of the specific heats of the two phases correct the heat of sublimation to room temperature using the procedure outlined in the second law treatment above.

Expanding equation (7) we have

$$\Delta_s H_{298} + \int_{298}^{T} C_{p(g)}dT - \int_{298}^{T_m} C_{p(c)}dT - \Delta H_f - \int_{T_m}^{T} C_{p(l)}dT$$

$$= T\left[S_{(g)T} - S_{(c)298} - \int_{298}^{T_m} C_{p(c)/T}dT - \frac{H_f}{T_m} - \int_{T_m}^{T} C_{p(l)/T}dt\right] \quad (8)$$

for the liquid-gas equilibrium. The suffixes c, l, g refer to crystal, liquid and gas respectively; ΔH_f is the heat of fusion, T_m the melting point and ΔH_{298} the heat of sublimation at room temperature.

For the solid-gas equilibrium, equation (7) becomes

$$\Delta_s H_{298} + \int_{298}^{T} C_{p(g)}dT - \int_{298}^{T} C_{p(c)}dT = T\left[S_{(g)T} - S_{(c)298} - \int_{298}^{T_m} C_{p(c)/T}dT\right] \quad (9)$$

For a diatomic gas, the entropy is given by the equation

$$S_T = \frac{3}{2} R\ln M + \frac{7}{2} R\ln T - R\ln P_{atm} + R\ln I - R\ln\sigma + Svib + S^o_e + 175.355$$

where M is the molecular weight, I the moment of inertia, Svib the vibrational entropy, S^o_e the entropy due to electronic transitions and σ the symmetry number (Se^o and $R\ln\sigma$ are zero for the alkali halides).

The specific heat of a diatomic gas is given by

$$C_{p(g)T} = 7/2\ R + C_{p(vib)}$$

where $C_{p(vib)}$ is the vibrational contribution to the specific heat at temperature T. A plot of $C_{p(vib)}$ against $1/T^2$ is approximately a straight line so that the total specific heat can be expressed by an equation of the form

$$C_{p(g)} = a - cT^{-2}$$

In order to be able to use the third law treatment to find the heat of sublimation at room temperature from a value of the vapour pressure over the liquid, we must have an accurate value of the entropy of the crystal at 298.16°K, we must know the specific heat equations of the solid and liquid, and the heat of fusion. Furthermore, we must know the vibration frequency of the gaseous molecule (for a diatomic gas) in order to calculate the vibrational contributions to the entropy and specific heat, and its internuclear distance in order to calculate the moment of inertia. If we are using the vapour pressure over the solid we obviously do not need the heat of fusion or the specific heat of the liquid.

The great strength of the third law treatment lies in its insensitivity to the value of the absolute pressure. If the pressure is in error by a factor of 2 at 1000°K the error in $\Delta_s H_{298}$ would be only 1 k.cal.

The second law treatment is very useful where there is insufficient data to be able to use the third law treatment.

The values of log p in the gaseous entropy terms of equations (8) and (9) were calculated from the values of Σ obtained at three temperatures, one at each end and one in the middle of the temperature range of the experiment, using the weighted mean values of $\Delta H'_o$ and I (equation (5)). Vapour pressure equations were calculated from these points.

CALIBRATION

The calibration substance chosen was potassium chloride since extensive data exist in the literature for the vapour pressures over both solid and liquid. The heat capacities of solid and liquid, the entropy of the crystal at room temperature, the heat of fusion and the vibrational frequency of the diatomic molecule are all well known so that it is possible to obtain accurate values of the heat of sublimation by both second and third law treatments. The data used in these calculations are given below

C_p crystal $= 9.89 + 5.20\times10^{-3}T + 0.77\times10^{5}T^{-2}$ cal/degC/mole (Reference Kelley (1949)).

C_p gas $= 8.94 - 2.23\times10^{4}T^{-2}$ (cal/degC/mole)

C_p liquid $= 16.00$ (cal/degC/mole) (Kelley(1949))

Heat of fusion = 6,100 cals/mole Kelley (1949)

Internuclear distance $= 2.6666\times10^{-16}$ Å Honig Mandel Stitch & Townes (1954)

Vibration frequency $= 281 cm^{-1}$ Rice & Klemperer (1957)[1]

Standard entropy of the gas at 1mm press $= 16.0148 \log_{10} T + 29.080 + S_{vib}$

Entropy of crystal at 298.16°K = 19.68 e.u. Strelkov (1954)

Using these data, the vapour pressure measurements from the literature were recalculated by the method outlined above in order to obtain values of the heat of sublimation by the

second and third law treatments. The results of these calculations are presented in Tables I and II.

It was originally intended to follow the procedure of Barrow et al (1955) with zinc, and Smith (1956) with cadmium which were used as calibration substances for the low temperature vapour pressure apparatus, and use the best third law value of the heat of sublimation to calculate the vapour pressure at the experimental temperatures and so calibrate the apparatus directly. It may be seen however, in Table I that in nearly all cases, the heat of sublimation from the third law treatment is smaller than that from the second law. The calibration runs carried out on this apparatus showed this trend also. As will be shown in a later section of this thesis, this trend may be explained by assuming the presence of dimers in the vapour. It was decided therefore to calibrate the graphite vessel using the absolute calibration constant calculated from the geometry of the vessel and the torsional constant of the quartz fibre.

The force on unit area of a surface due to bombardment by gas molecules is equal to the change in momentum in unit time of the molecules striking it. Since the molecules make elastic collisions at the surface, the force per unit area (in fact the pressure of the gas) is equal to twice the momentum of the gas molecules striking it in unit time. If the molecules leave the vessel through a hole of unit area,

TABLE I

KCl solid

Reference	n	temp °K	$\Delta_s H_{298}$ kcal/mole second law	third law
Deitz	11	847-936	53.96 ± 0.99	53.1
Mayer and Wintner	5	899-935	57.58 ± 4.99	52.7
Niwa	11	853-955	51.62 ± 0.54	52.8
Zimm and Mayer	21	624-945	52.99 ± 0.64	52.7
Treadwell and Wernher	13	859-1024	53.94 ± 0.12	52.8
Bradley and Volans	27	712-870	54.06 ± 0.50	52.8
Miller and Kusch	10	872-967	53.65 ± 1.76	51.9
Present work (quartz cell)		819-893	53.50 ± 0.82	52.7

TABLE II

KCl liquid

Reference	n	temp °K	$\Delta_s H_{298}$ kcal/mole second law	third law
Wartenburg & Albrecht	16	1390-1695	51.62 ± 1.42	53.1
Flock and Rodebush	9	1179-1378	52.68 ± 0.42	53.0
Jackson and Morgan	3	1074-1317	42.21 ± 6.91	52.6
Kangro and Wieking	3	1133-1263	43.34 ±15.24	51.6
Horiba and Baba	10	973-1524	46.36 ± 1.31	51.5
Ruff and Mugdan	7	1393-1688	55.23 ± 1.47	53.2
Barton and Bloom	11	1280-1540	52.7 ± 0.4	52.9
Kordes and Raaz	1	1684		52.8
Bergstrom	1	1773		54.8
Greiner and Jellinek	1	1180		50.2

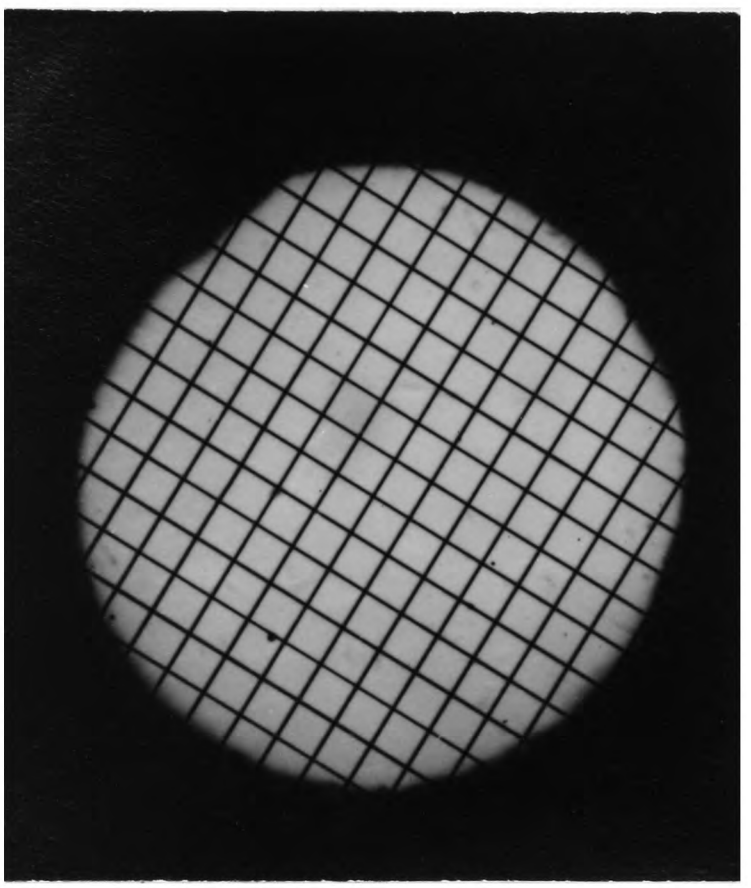


Fig. 9

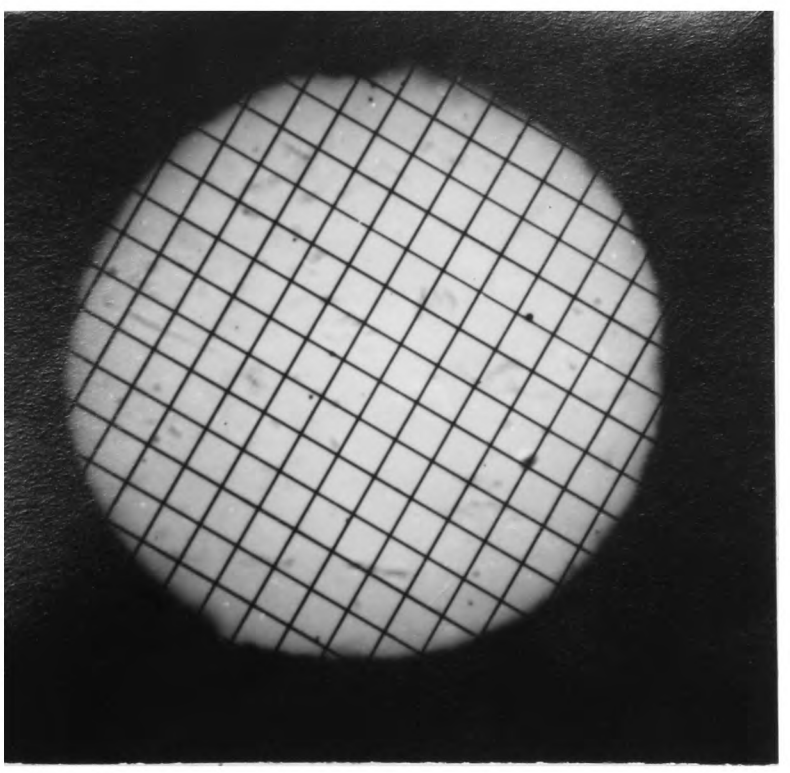


Fig. 10

the force exerted on the vessel will be equal to the momentum of the molecules passing through the hole in unit time i.e. to half the pressure.

The couple exerted on the vessel due to effusion of gas at a pressure p through holes of areas a_1 and a_2 at distances l_1 and l_2 from the axis of rotation is balanced at equilibrium by the couple exerted by the twisted quartz fibre

$$\tfrac{1}{2} p (a_1 l_1 f_1 + a_2 l_2 f_2) = c\theta$$

where f_1, f_2 are factors related to the ratio (depth of hole/ radius of hole) c is the torsional constant of the quartz fibre. θ is the angle through which the fibre is twisted.

The areas of the holes were found micro-photographically. A photograph of each hole was taken using a microscope with a 2/3" objective and a projection eyepiece. The image of a grating in the eyepiece was superimposed on the image of the hole. The area of one square of the grating was found by taking a separate photograph of a standard millimeter divided into hundredths. The hole was strongly illuminated by light from a microscope lamp reflected by a piece of white paper placed in the end of the vessel. The photographs of the holes were enlarged and their areas measured with a planimeter. Figures 9 and 10 are contact prints of the photographs of the holes.

The thickness of each hole was found using a microscope.

The microscope was focussed first on the top and then on the bottom of the hole using the fine focus adjustment. The number of revolutions of the fine focus knob between these two positions was found from a paper scale attached to the knob. The fine focus adjustment was calibrated by focussing the microscope on first the top and then the bottom surface of a microscope slide using the fine focus adjustment. The thickness of the microscope slide was found using a micrometer.

Since the effusion holes and the hole for the suspension rod had been accurately drilled to lie in planes at right angles to each other with the hole for the suspension rod through the centre of the vessel it was assumed that the major axis of the vessel, when suspended, would be horizontal, and accordingly it was necessary only to measure the distance of each hole from the suspension rod. This was carried out in the lathe. A sharp pointer was clamped in the micrometer tool rest of the lathe; the vessel was clamped in the chuck of the head stock; the tool rest carriage was clamped to the bed of the lathe so that only by moving the micrometer slide could the pointer be moved. The micrometer was adjusted until the pointer lay just over the effusion hole, the chuck was turned through a right angle and the micrometer adjusted until the pointer lay over the centre of the suspension rod. The difference between the two micrometer readings gave the distance of the hole from the axis of rotation. It was found

possible to obtain distances reproducible to $\pm$ .002." (The author is indebted to Mr. F. March for suggesting the method).

The factor f is analagous to the Clausing factor used to correct for the thickness of the hole in weight loss effusion experiments. The reaction on a vessel due to effusion of gas through a channel hole has been investigated by Freeman (1954) who tabulates values of f for various ratios of thickness to radius of hole. His results are plotted in Figure 11 and were used to obtain values of f in determining the absolute calibration constant of the graphite vessel.

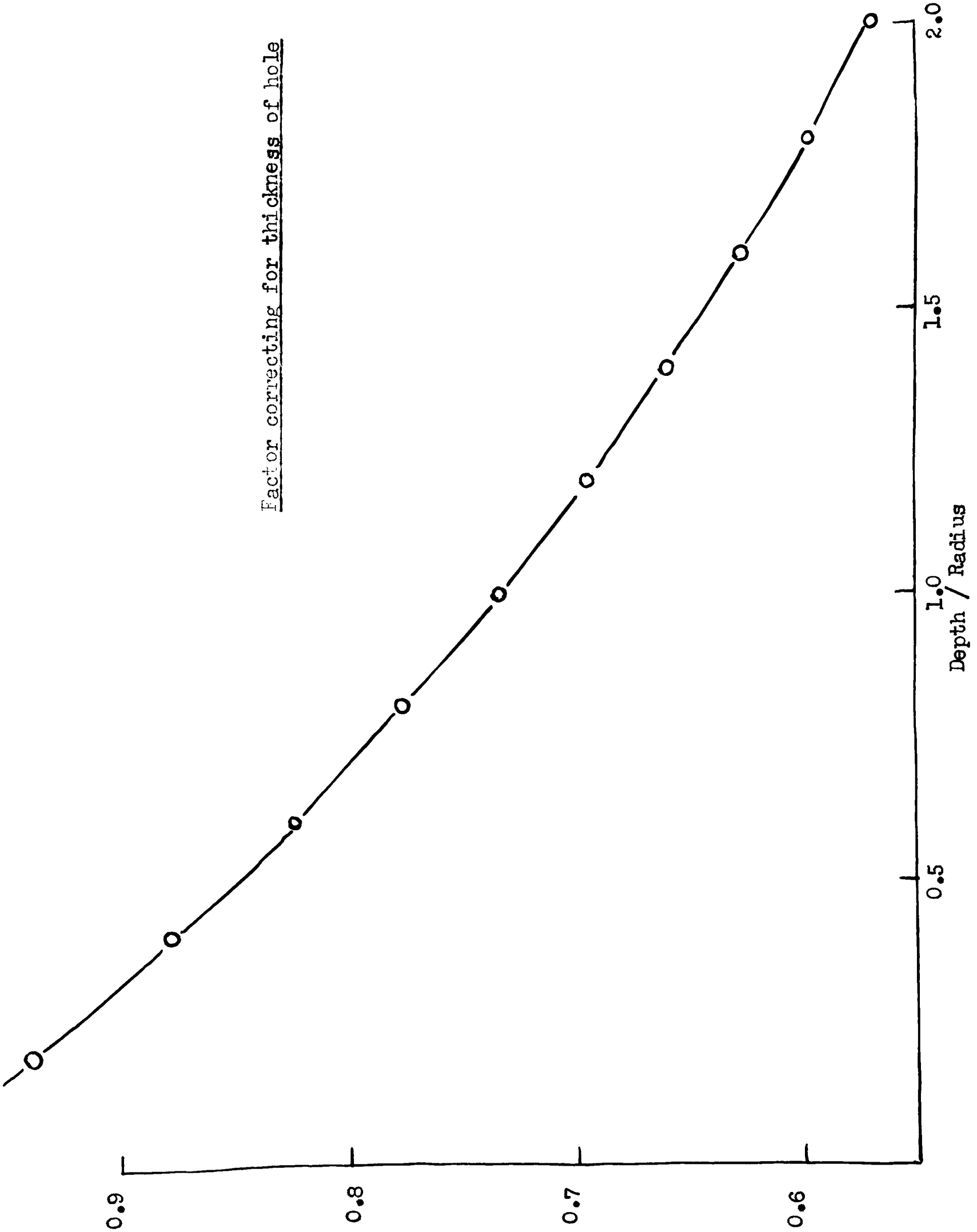
The torsional constant (c) of the fibre was found by suspending from it a small Dural bar whose moment of inertia (I) was accurately known from its dimensions and measuring the period of oscillation (T). These quantities are related by the formula

$$T = \frac{1}{2\pi}\sqrt{\frac{I}{C}}.$$

The following is a summary of the measurements on graphite vessel number 4 and fibre number 3.

	Hole A	Hole B
Area	.2978 sq.mm.	.3014 sq.mm.
Thickness	0.12 mm	0.18 mm
Distance from axis	1.425 cm	1.334 cm
f	0.885	0.837

Fig. 11


Factor correcting for thickness of hole
0.9
0.8
0.7
0.6
0.5
1.0
1.5
2.0
Depth / Radius

Moment of inertia of Dural bar 3.0282 gr.cm^2.
Period of oscillation 82.4 secs.
Force constant of fibre 1.761 x 10^{-2} dynes/radian.

The calibration constant was 3.709x10^{-3}mm Hg/radian. Since the angle moved through by the spot of light reflected from the mirror on the suspension is double that moved through by the suspension, the calibration constant is 1.855mm Hg/radian of deflection of spot of light.

This value of the calibration constant was corrected for thermal expansion of the holes at the mid-temperature of any run, using the coefficient of expansion given in the Handbook of Chemistry and Physics. The change in hole area over the range of a run is negligible.

Discussion of Calibration constant.

Whitman (1952) discussed the dimensions of effusion cells and gave the following conditions which must be satisfied if the actual rate of effusion is to agree with that calculated from Kinetic Theory:

1) the molecules collide only with the walls of the vessel.

2) Reflection after such collisions is diffuse.

3) The molecules enter the effusion hole with the cosine distribution of directions.

4) The molecules enter uniformly over the face of the effusion hole.

Condition (1) requires that the dimensions of the effusion cell shall be not more than one tenth of the mean free path of the gas under the conditions of the experiment.

Taking the collision diameter of potassium chloride as 4.0Å, the mean free path at 850°K and 10^{-3}mm is 11.1cm. The diameter of the effusion hole and the dimensions of the effusion cell should be less than 1.1cm. This condition is satisfied for the graphite cell for this temperature and pressure. At 3×10^{-2}mm, (the highest pressure measured), and a temperature of 950°K, the mean free path is only 1.2cm. Under these conditions, the diameter of the hole is still less than one tenth of the mean free path, so that there will be few molecular collisions within the hole; but the dimensions of the cell are now of the order of the mean free path. This is considered to be not as important as the condition that the diameter of the effusion hole should be small compared with the mean free path. Searcy and Freeman (1954) used an effusion vessel of similar dimensions with holes four times the diameter of those used here at a pressure of 6×10^{-2}mm without apparently increasing the scatter in their results.

It seems probable that condition (2) will be fairly well satisfied for the rather rough graphite walls of the cell. Conditions (3) and (4) will be fairly well satisfied since the diameter of the effusion hole is less than one tenth that of the cell. In any case, Whitman considers that errors due to these conditions not being satisfied will be small.

The gas pressure in the space surrounding the effusion

vessel must be less than the permissible error in measuring the absolute vapour pressure. In the present work the lowest pressures measured were about 4×10^{-4} mm. The residual pressure in the apparatus was often less than 5×10^{-6} for these pressure readings, so that the absolute error in the measurements due to this cause should not be greater than one or two per cent.

It is important that the effusion hole should be small, for reasons apart from those associated with the mean free path.

It is necessary to assume that loss of molecules from the vessel will not disturb the equilibrium between the vapour and the condensed phase. Speiser and Johnston have examined this assumption with respect to the hole size and the vapourisation coefficient from the condensed phase. They showed that

$$P_{obs} = P_{true} \left(\frac{\alpha}{a/s + \alpha} \right)$$

where α = vapourisation coefficient (i.e. the ratio of the number of molecules vapourising from a surface to the theoretical number calculated from kinetic theory)

a = area of hole

s = effective area of condensed phase.

It is important therefore that the ratio a/s should be small. This condition has been achieved in the present apparatus.

Littlewood and Rideal (1956) have shown that low values of the vapourisation coefficient can be caused by surface cooling of the condensed phase. In the case of good conductors such as metals, the heat of sublimation is rapidly conducted to the surface so that the surface remains very close to the temperature of the surroundings. For poor conductors the surface cooling is much greater and the apparent vapourisation coefficient is too small. The apparent vapourisation coefficient falls as the rate of evaporation increases. By using small holes and a sensitive fibre, the surface cooling is kept to a minimum. Searcy and Freeman (1954) used a torsion-effusion method of measuring the vapour pressure of tin. They used holes 2.4mm in diameter and their highest pressure was 6×10^{-2} so that the rate of evaporation must have been large. However, since tin is a good conductor no error was apparently introduced by these high evaporation rates. The alkali halides being poor conductors, it was essential to keep the evaporation rate low.

Calibration runs on potassium chloride.

In Tables III to XI are given the results of the runs on samples of 'Analar' potassium chloride. Three vessels were used: quartz, graphite and platinum which are denoted by the letters Q, G and Pt in the run number. The column

headings are as follows.

Log D = log deflection of spot of light from zero positions in centimetres.

$T^{\circ}K$ = absolute temperature

$10^3/T$

Σ

see page 42

I

The second law value of the heat of sublimation at $298^{\circ}K$ and the 95% confidence limits for the run are given at the foot of each table.

The results are collected in Table XII where the weighted mean values of the heat of sublimation by the second law treatment are compared with the mean value from the third law treatment, for each vessel used.

For the graphite vessel

$$\text{Log } p_{mm} = \text{Log } D_{cm} - 4.740$$

For the platinum vessel

$$\text{Log } p_{mm} = \text{Log } D_{cm} - 4.421$$

In Figure 12 the results obtained are plotted on a graph with those of other authors. As can be seen, the results are in satisfactory agreement.

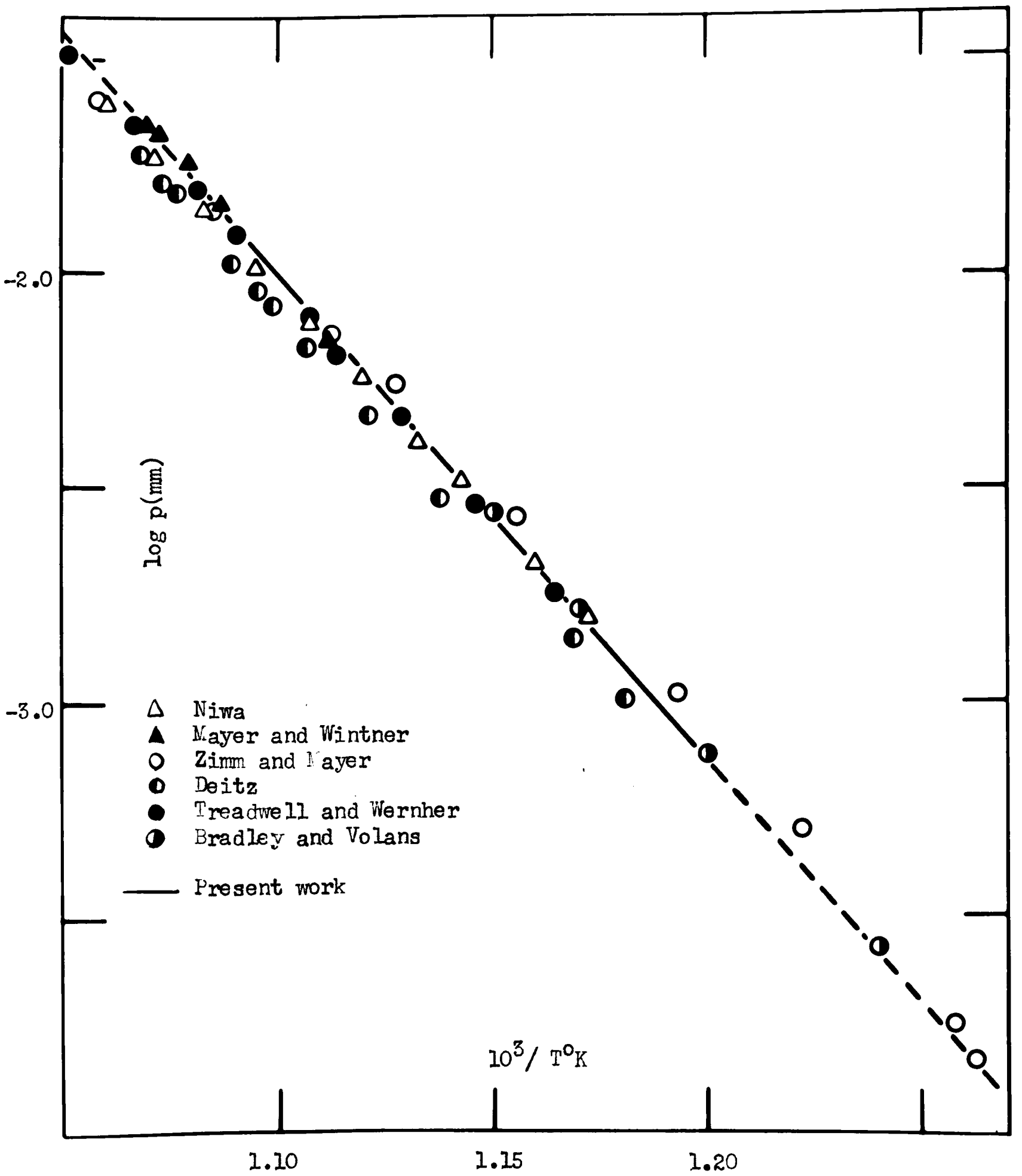

-2.0
-3.0
Log p(mm)
Niwa
Mayer and Wintner
Zimm and Mayer
Deitz
Treadwell and Wernher
Bradley and Volans
Present work
10³/ T°K
1.10
1.15
1.20

Fig. 12

TABLE III

Run 3-20 (iii) KCl

Log D	T.	$\frac{10^3}{T}$	Σ	I"
2.2390	892.1	1.1210	4.1700	17.4150
2.2317	891.8	1.1213	4.1624	17.4109
2.1951	889.2	1.1246	4.1239	17.4114
2.1614	887.1	1.1273	4.0885	17.4079
2.1471	886.4	1.1282	4.0737	17.4038
2.1310	884.7	1.1303	4.0562	17.4111
2.0892	881.8	1.1340	4.0124	17.4110
2.0611	879.9	1.1365	3.9827	17.4108
2.0484	879.0	1.1377	3.9693	17.4116
2.0831	881.4	1.1346	4.0058	17.4115
2.0611	879.9	1.1365	3.9827	17.4108
2.0073	876.1	1.1414	3.9259	17.4119
1.9689	873.5	1.1448	3.8855	17.4117
1.9106	869.5	1.1501	3.8242	17.4130
1.8751	866.9	1.1535	3.7722	17.4012
1.8089	862.3	1.1597	3.7178	17.4200
1.7566	859.5	1.1635	3.6623	17.4094
1.7202	857.1	1.1667	3.6240	17.4089
1.6646	853.3	1.1719	3.5655	17.4119
1.6138	850.2	1.1764	3.5124	17.4120
1.5763	847.6	1.1798	3.4729	17.4126
1.3997	836.7	1.1952	3.2878	17.4095
1.3324	832.1	1.2018	3.2168	17.4165
1.2648	828.6	1.2069	3.1465	17.4064
1.2355	826.4	1.2101	3.1155	17.4132
1.2304	826.2	1.2104	3.1102	17.4115
1.2227	825.5	1.2114	3.1020	17.4151
1.1847	833.7	1.2140	3.0625	17.4063
1.1072	819.3	1.2206	2.9816	17.4034
1.1139	819.2	1.2207	2.9883	17.4113
1.1106	818.9	1.2212	2.9847	17.4135

ΔH_{298} = 53.88 kcal/mole

95% Confidence Limit 0.19 kcal/mole

TABLE IV

RUN 3 2Q (iv) KCl

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.2276	891.6	1.1216	4.1583	17.2983
2.2154	890.6	1.1228	4.1452	17.2993
2.2143	890.6	1.1228	4.1441	17.2982
2.2415	892.8	1.1201	4.1731	17.2955
2.2330	892.1	1.1210	4.1640	17.2970
2.1664	887.3	1.1270	4.0937	17.2970
2.1351	885.2	1.1297	4.0607	17.2956
2.1274	884.7	1.1303	4.0526	17.2945
2.0748	881.1	1.1349	3.9973	17.2931
2.0342	878.3	1.1386	3.9545	17.2937
2.0269	877.6	1.1395	3.9467	17.2964
1.9689	873.6	1.1447	3.8856	17.7962
1.8675	866.6	1.1539	3.7787	17.2971
1.8162	863.1	1.1586	3.7247	17.2982
1.4843	841.7	1.1881	3.3763	17.2953
1.4487	839.3	1.1915	3.3388	17.2977
1.4082	836.9	1.1949	3.2963	17.2950
1.2856	829.1	1.2061	3.1677	17.2976
1.2553	827.5	1.2085	3.1362	17.2943
1.2553	827.2	1.2089	3.1359	17.2986

$\Delta\ {}_{s}H_{298} = 53.43$ kcal/mole

95% Confidence Limit = 0.12 kcal/mole

TABLE V

RUN 3 20 v KCl

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.2475	893.5	1.1191	4.1795	17.2454
2.2453	893.3	1.1194	4.1773	17.2467
2.2410	893.3	1.1194	4.1730	17.2424
2.1962	889.9	1.1237	4.1255	17.2451
2.1562	887.1	1.1273	4.0833	17.2450
2.1380	885.9	1.1288	4.0642	17.2434
2.1313	885.4	1.1294	4.0571	17.2433
2.0980	882.9	1.1326	4.0219	17.2455
2.0488	879.5	1.1370	3.9701	17.2450
1.9952	875.9	1.1417	3.9137	17.2435
1.9609	873.5	1.1448	3.8775	17.2435
1.8797	867.8	1.1523	3.7919	17.2455
1.8331	864.7	1.1565	3.7429	17.2455
1.7987	862.3	1.1597	3.7066	17.2466
1.7694	860.4	1.1623	3.6759	17.2462
1.6551	852.8	1.1726	3.5557	17.2463
1.5933	849.0	1.1779	3.4909	17.2434
1.4829	841.7	1.1881	3.3749	17.2464
1.4346	838.1	1.1932	3.3237	17.2458
1.3802	835.0	1.1976	3.2669	17.2494
1.3692	834.8	1.1979	3.2558	17.2418
1.3345	832.6	1.2011	3.2193	17.2426
1.3243	832.4	1.2013	3.2090	17.2347
1.3181	831.2	1.2031	3.2017	17.2484
1.2788	829.2	1.2060	3.1610	17.2415

$\Delta_s H_{298}$ = 53.24 kcal/mole

95% Confidence Limit = 0.22 kcal/mole.

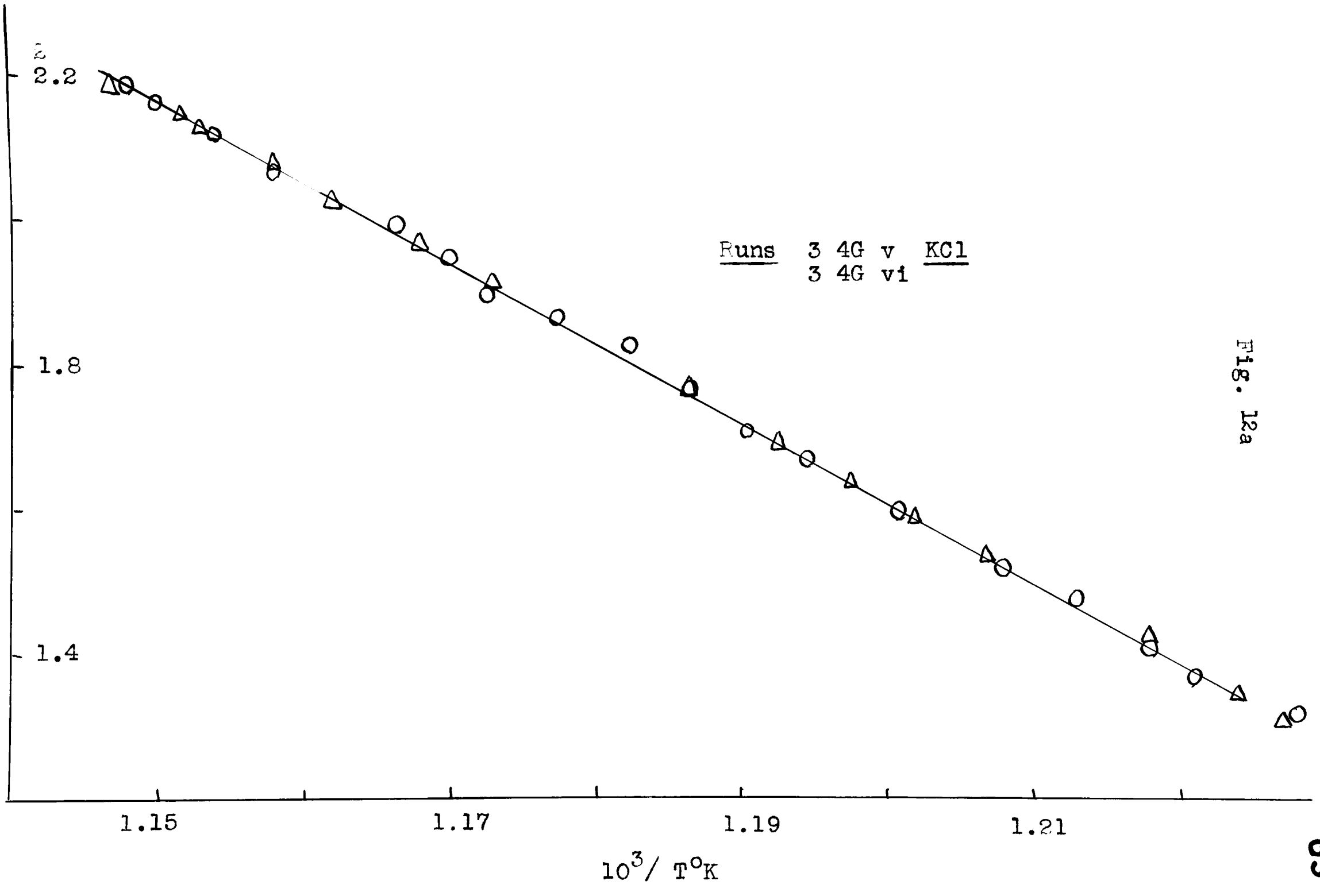


Fig. 12a

TABLE VI

RUN 3 4G (v) KCl

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.1850	871.1	1.1480	4.0997	17.3506
2.1626	869.7	1.1498	4.0763	17.3480
2.1216	866.6	1.1539	4.0328	17.3518
2.0734	863.3	1.1583	3.9822	17.3520
1.9991	857.3	1.1664	3.9031	17.3664
1.9518	854.7	1.1700	3.8539	17.3588
1.8993	852.8	1.1726	3.7999	17.3350
1.8681	849.3	1.1774	3.7660	17.3563
1.8149	845.7	1.1825	3.7099	17.3590
1.7664	842.8	1.1865	3.6593	17.3546
1.7093	839.5	1.1912	3.5995	17.3491
1.6730	836.9	1.1949	3.5611	17.3534
1.5999	832.1	1.2018	3.4843	17.3562
1.5250	827.6	1.2083	3.4060	17.3529
1.4786	824.5	1.2129	3.3571	17.3571
1.4133	821.1	1.2179	3.2892	17.3470
1.3692	818.2	1.2222	3.2428	17.3502
1.3201	814.6	1.2276	3.1909	17.3606
1.2304	810.1	1.2344	3.0976	17.3458

$\Delta_s H_{298}$ = 52.64 kcal/mole

95% Confidence Limit = 0.58 kcal/mole

TABLE VII

RUN 3 4G (v1) KCl

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.1884	871.6	1.1473	4.1036	17.4538
2.1467	868.3	1.1517	4.0594	17.4608
2.1303	867.1	1.1533	4.0420	17.4620
2.0788	863.5	1.1581	3.9877	17.4635
2.0346	860.4	1.1623	3.9411	17.4658
1.9717	856.2	1.1680	3.8749	17.4659
1.9186	852.8	1.1726	3.8192	17.4638
1.7679	842.8	1.1865	3.6607	17.4670
1.6946	838.3	1.1929	3.5839	17.4647
1.6415	835.0	1.1976	3.5282	17.4637
1.5922	831.9	1.2021	3.4765	17.4643
1.5353	828.6	1.2069	3.4169	17.4606
1.4133	821.1	1.2179	3.2892	17.4609
1.3464	817.0	1.2240	3.2190	17.4617
1.3118	814.9	1.2271	3.1828	17.4615

$\Delta_{s}H_{298}$ = 53.06 kcal/mole

95% Confidence Limit = 0.46 kcal/mole

TABLE VIII

RUN 3 4G (v11) KCl

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.1940	871.9	1.1469	4.1093	17.3276
2.1892	871.4	1.1476	4.1043	17.3306
2.1303	867.3	1.1530	4.0421	17.3307
2.0910	864.5	1.1567	4.0007	17.3319
2.0492	861.6	1.1606	3.9566	17.3328
2.0208	859.5	1.1635	3.9266	17.3362
1.9619	855.2	1.1693	3.8643	17.3407
1.9138	852.1	1.1736	3.8139	17.3399
1.8519	848.4	1.1787	3.7490	17.3338
1.8075	845.2	1.1832	3.7022	17.3388
1.7634	842.4	1.1871	3.6559	17.3375
1.7016	838.6	1.1925	3.5912	17.3350
1.6551	835.7	1.1966	3.5424	17.3335
1.6064	832.4	1.2013	3.4911	17.3364
1.5502	828.9	1.2064	3.4321	17.3361
1.5289	827.7	1.2082	3.4099	17.3347
1.4857	825.3	1.2117	3.3649	17.3300
1.4362	822.0	1.2165	3.3128	17.3332
1.2945	813.8	1.2288	3.1646	17.3268

ΔH_{298} = 52 .56 kcal/mole

95% Confidence Limit = 0.36 kcal/mole

Fig. 12b

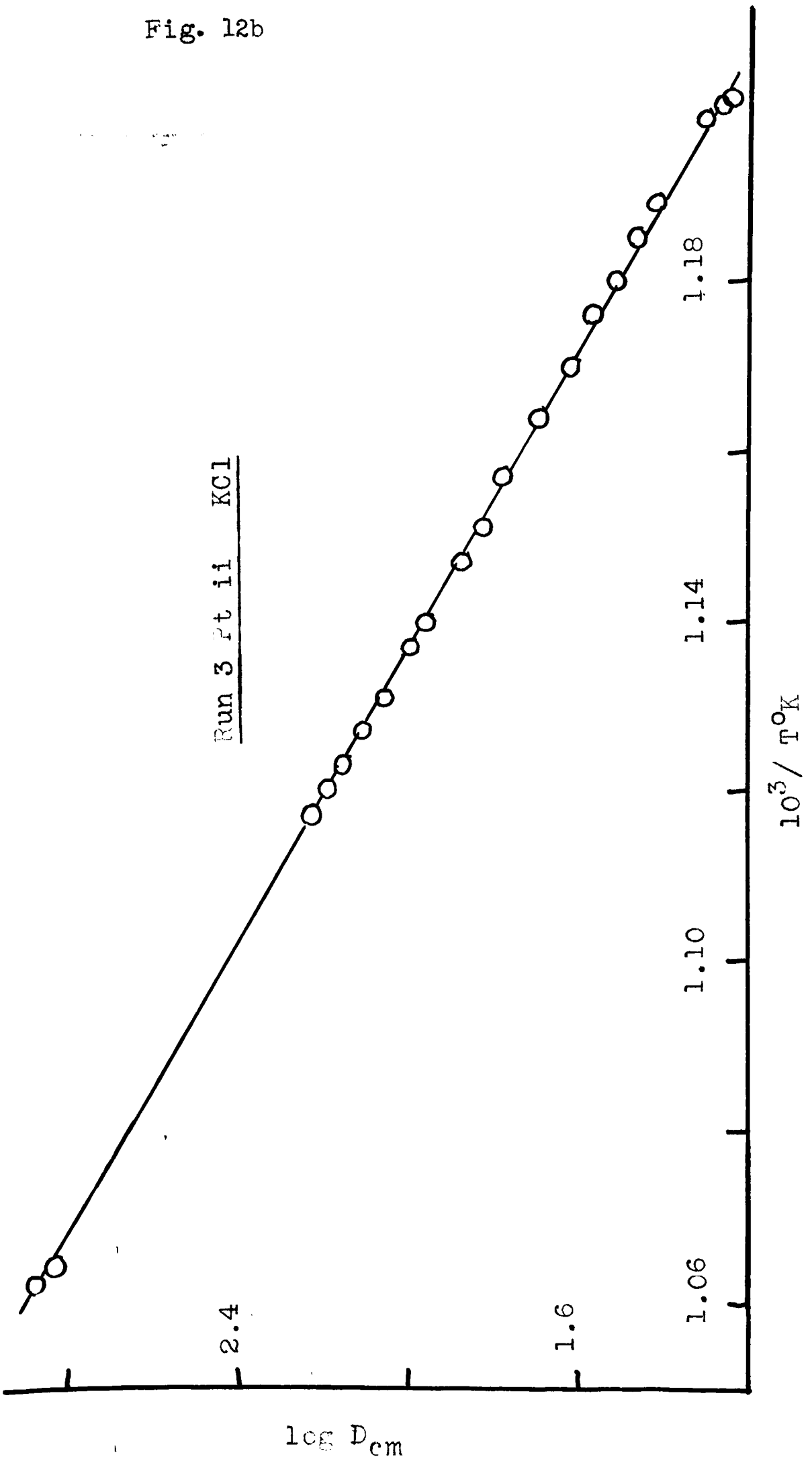


TABLE IX.

Run 3Pt (1) KCl.

Log D	T	Σ	$\frac{10^3}{T}$	I"
2.8749	942.9	4.8449	1.0606	17.5970
2.8747	942.9	4.8447	1.0606	17.5968
2.8469	940.8	4.8152	1.0629	17.5950
2.8200	938.2	4.7863	1.0659	17.6021
2.8042	937.0	4.7696	1.0672	17.6011
2.2797	900.1	4.2168	1.1110	17.5749
2.2526	898.2	4.1883	1.1133	17.5741
2.2044	894.7	4.1373	1.1177	17.5760
2.1864	893.3	4.1183	1.1196	17.5798
2.0878	886.1	4.0141	1.1285	17.5826
2.0554	883.0	3.9794	1.1325	17.5960
2.0175	881.4	3.9402	1.1346	17.5821
1.9750	878.6	3.8955	1.1382	17.5806
1.9420	876.0	3.8606	1.1416	17.5866
1.9009	873.1	3.8172	1.1453	17.5877
1.7218	860.8	3.6286	1.1617	17.5963
1.6981	859.2	3.6037	1.1639	17.5979
1.6274	854.7	3.5295	1.1700	17.5970
1.5977	852.5	3.4981	1.1730	17.6017
1.5694	850.4	3.4681	1.1759	17.6065

$\Delta_s H_{298}$ = 54.84 Kcal/mole.

95% confidence limit = 0.58 Kcal/mole.

TABLE X.

Run 3Pt (11) KCl.

Log D	T	Σ	$\frac{10^3}{T}$	I"
2.8443	941.3	4.8130	1.0624	17.4503
2.8457	941.3	4.8144	1.0624	17.4517
2.8463	941.5	4.8152	1.0624	17.4489
2.8263	939.4	4.7936	1.0645	17.4558
2.2266	895.4	4.1601	1.1168	17.4444
2.1912	893.0	4.1229	1.1198	17.4429
2.1529	890.4	4.0825	1.1231	17.4418
2.1059	887.3	4.0331	1.1270	17.4388
2.0622	884.2	3.9871	1.1310	17.4404
1.9912	879.3	3.9123	1.1373	17.4405
1.9562	876.9	3.8755	1.1404	17.4406
1.8745	871.5	3.7895	1.1474	17.4378
1.8215	867.9	3.7339	1.1522	17.4393
1.7782	864.6	3.6880	1.1566	17.4458
1.6946	859.4	3.6002	1.1636	17.4412
1.6191	854.2	3.5208	1.1707	17.4463
1.5563	850.4	3.4550	1.1759	17.4423
1.5132	847.6	3.4098	1.1798	17.4435
1.4594	843.8	3.3530	1.1851	17.4498
1.4166	841.2	3.3082	1.1888	17.4490
1.3010	833.8	3.1869	1.1993	17.4526
1.2553	831.0	3.1389	1.2034	17.4534
1.2430	830.0	3.1258	1.2048	17.4569

$\Delta_s H_{298}$ = 54.25 Kcal/mole.

95% confidence limit = 0.25 Kcal/mole.

TABLE XI.

Run 3Pt (111) KCl.

Log D	T	Σ	$\frac{10^3}{T}$	I"
2.9008	945.3	4.8725	1.0579	17.3753
2.9058	945.3	4.8775	1.0579	17.3803
2.2702	898.4	4.2060	1.1131	17.3611
2.2175	894.9	4.1506	1.1174	17.3566
2.1784	892.1	4.1094	1.1210	17.3579
2.1136	887.8	4.0414	1.1264	17.3537
2.0398	882.3	3.9632	1.1334	17.3783
1.9699	877.6	3.8897	1.1395	17.3569
1.8739	871.2	3.7886	1.1478	17.3538
1.8169	867.2	3.7287	1.1531	17.3566
1.7796	864.6	3.6893	1.1566	17.3586
1.7226	860.8	3.6296	1.1617	17.3591
1.6304	854.7	3.5325	1.1700	17.3601
1.5966	852.0	3.4965	1.1737	17.3678
1.4065	840.0	3.2971	1.1905	17.3670
1.3692	837.1	3.2576	1.1946	17.3760
1.3222	834.3	3.2084	1.1986	17.3740
1.2742	831.3	3.1581	1.2029	17.3745

$\Delta_s H_{298}$ = 53.90 Kcal/mole.

95% confidence limit = 0.49 Kcal/mole.

TABLE XII

POTASSIUM CHLORIDE

Run	n	temp°K	$\Delta_s H_{298}$ kcal/mole second law	third law
3 2Q iii	31	819-892	53.[illegible] ± 0.19	
3 2Q iv	20	829-893	53.43 ± 0.11	
3 2Q v	25	827-892	53.24 ± 0.22	
mean			53.50 ± 0.82	
3 4G v	19	810-871	52.64 ± 0.58	
3 4G vi	15	814-872	53.06 ± 0.46	
3 4G vii	19	814-872	52.56 ± 0.36	
mean			52.73 ± 0.67	52.7
3 Pt i	20	850-943	54.83 ± 0.58	
3 Pt ii	23	930-941	54.25 ± 0.25	
3 Pt iii	18	831-945	53.90 ± 0.49	
mean			54.26 ± 1.18	52.7
weighted mean of all runs			53.63	52.7

$$\log p(\text{mm}) = 10.455 - 11324/T$$

PART II

THE VAPOUR PRESSURES OF THE ALKALI FLUORIDES

Introduction.

Introduction.

The boiling points of the liquid alkali fluorides have been measured at a series of pressures by Ruff Schmidt and Mugdan (1922) and v.Wartenburg and Schulz (1921). Both suspended a small bucket containing the salt from a sensitive spring balance and observed the boiling point by the sudden rapid change of weight.

Measurements on the vapour pressure over the solid crystal are less numerous. Niwa has measured the vapour pressure of solid sodium fluoride and potassium fluoride using a weight-loss effusion method. There is an isolated observation for sodium fluoride by Ryan and Twichell. Recently Sense et al (1957) have used a transpiration method for sodium fluoride crystal and liquid. Miller and Kusch (1956) in their molecular beam experiments have obtained values of the vapour pressure sodium fluoride which are not very accurate because of difficulties in estimating the slit area at high temperatures. No data at all exist for the vapour pressures of solid lithium fluoride, or rubidium fluoride or caesium fluoride.

Preparation of materials.

It is important that pure materials should be used. Commercial samples of sodium fluoride and lithium fluoride labelled "extra pure" were tried but were not found satisfactory.

Lithium fluoride of the highest purity is used for windows in ultra violet spectroscopy. The sample of lithium fluoride used was obtained by powdering a fragment of a broken window.

The remaining alkali fluorides were prepared by adding a very slight excess of Analar hydrofluoric acid to the alkali carbonate in a platinum dish, evaporating to dryness and then strongly heating the residue to decompose any bifluoride which might be present. Simons (1950) states that caesium bifluoride, the most stable bifluoride is completely dissociated to caesium fluoride and hydrogen fluoride at 500-600°C. Potassium, rubidium and caesium fluorides are extremely deliquescent so were kept in a vacuum desiccator.

Thermo chemical data.

Table XIII below gives the thermochemical data used in calculating the heats of sublimation of the alkali fluorides.

Table XIII

	C_p crystal								
	a	bx10^3	cx10^{-5}	Ref.	ΔH_f cal	T_m °K	Ref.	S^o_{298} e.u.	Ref.
LiF	10.85	3.21	1.60	1	6471	1121.3	1	8.52	1,5,6
NaF	9.66	4.50	-	2	7780	1265	2	12.26	3
KF	11.02	3.12	"	2	6750	1130	2	15.91	7
RbF	11.94*	2.37*	-	4	(6300)	1048	8	17.4*	9
CsF	11.3*	2.71*	-	4	(5700)	955	8	19.1*	9

a, b and c are the constants in the specific heat equation $C_p = a + bT - cT^{-2}$; ΔH_f is the heat of fusion; T_m is the melting point and S^o_{298} the standard entropy of the crystal.

	C_p liquid	Ref.	C_p gas a	C_p gas cx10^{-4}	ω_e cm^{-1}	Ref	r_e Å	Ref
LiF	15.51	1	8.81	11.6	773*	10	1.527*	12
NaF	16.00	2	8.92	6.62	500*	11	1.840*	12
KF	16.00	2	8.88	4.42	(400)		2.129*	12
RbF	(16.0)		8.93	4.42	389*	11	2.246*	12
CsF	(16.0)		8.93	3.92	360	11	2.3453	12

References.

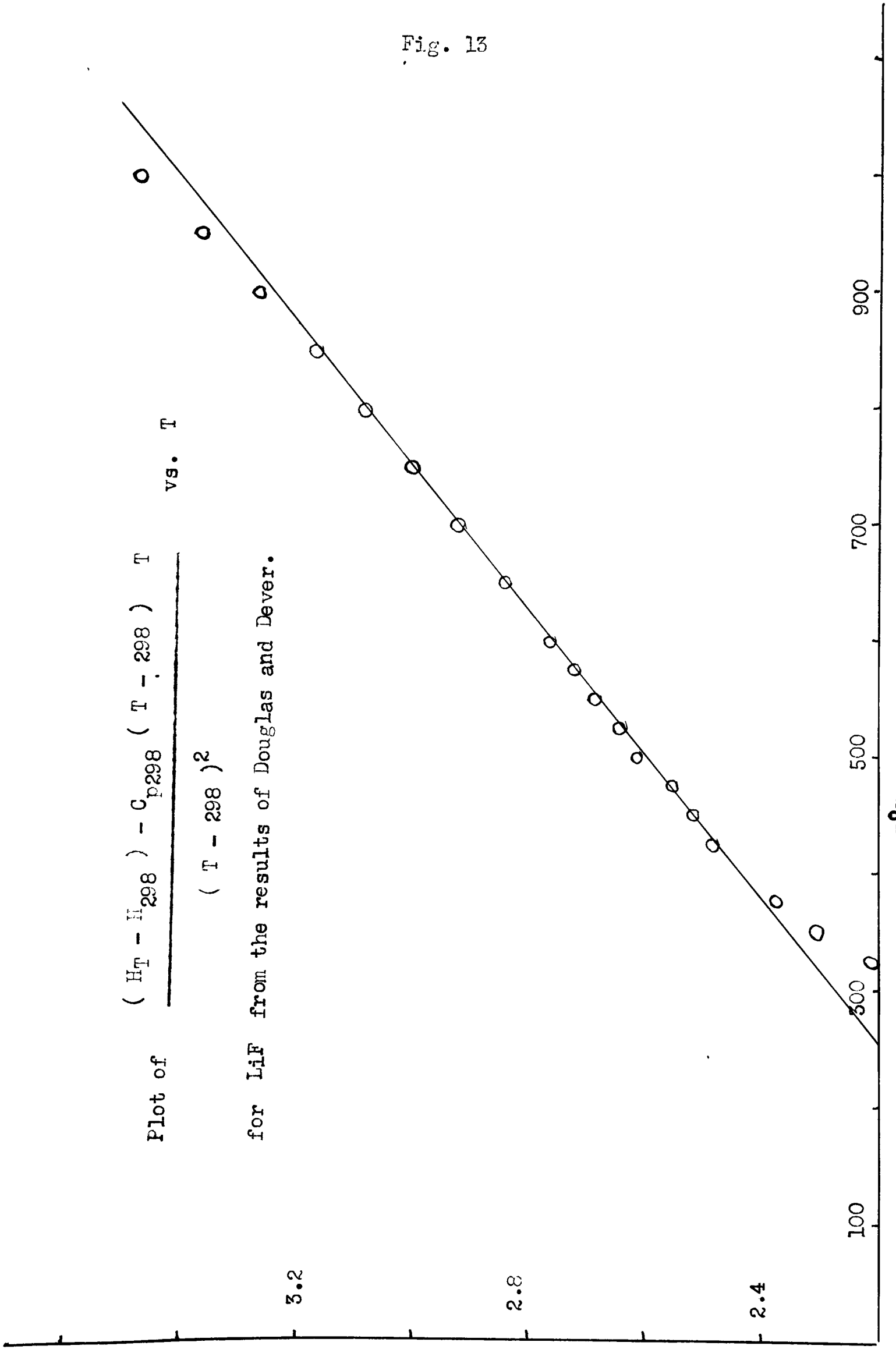
1. Douglas and Dever (1954)
2. Kelley (1949)
3. King et al (1957)
4. Kubachewski and Evans (1956)
5. Clusius et al (1949)
6. Voskresenskaya (1956)
7. Westrum and Pitzer (1949)
8. Brewer (1950)
9. Latimer (1951)
10. Rittner (1951)
11. Klemperer (1957)
12. Honig et al (1954)

Notes:- The quantities in brackets have been estimated by the author; other estimated quantities are marked by an asterisk.

Douglas and Dever (1954) measured the specific heat of lithium fluoride. Their results have been fitted to the three constant equation using the method given by Kelley (1949). The curve produced is shown in Figure 13. As can be seen, the linearity is excellent over most of the temperature range though there is a slight curvature at each end. Westrum and Pitzer have measured the heat capacity of potassium fluoride very accurately. Their results are in reasonable agreement with those given in Kelley (1949), but since their maximum temperature was 500$^{o}_{K}$ Kelley's equation was used.

The heats of fusion of rubidium fluoride and caesium fluoride quoted by Kelley (1936) were not considered very

Fig. 13


Plot of $\frac{(H_T - H_{298}) - C_{p298}(T - 298)}{(T - 298)^2}$ vs. T
for LiF from the results of Douglas and Dever.
3.2
2.8
2.4
100
300
500
700
900
T°K

trustworthy. They were measured, using a two component system, by Puschin and Baskow (1913). This method is known to be prone to error since the activity coefficients of the two salts are not known. Comparison of their values for the other alkali fluorides with accepted values shows that all their results are low. Kubachewski and Evans (1956) state that the entropy of fusion for similar types of substance should be roughly the same. The entropy of fusion of the other alkali fluorides is close to $6_{e.u}$/mole and this value was used in estimating the heats of fusion of rubidium fluoride and caesium fluoride.

The only directly measured vibration frequency of the diatomic gaseous molecule is that for caesium fluoride, measured by Klemperer (1957) from studies of the infra red spectrum. He has determined the vibration frequencies for other alkali halides and finds that for the halides of any one metal a plot of force constant against the ionisation potential of the halogen is a straight line. The extrapolation to the fluoride in the case of caesium gives excellent agreement with the experimental frequency. The extrapolation has been used for the fluorides of sodium and rubidium. A mean of the vibration frequencies for potassium fluoride given by Barrow and Caunt (1953) Grabner and Hughes (1950) and Klemperer's (1957) extrapolation was used. Klemperer's extrapolation does not work for lithium fluoride, and Kittner's (1951) value for the vibration frequency was used.

Experimental results.

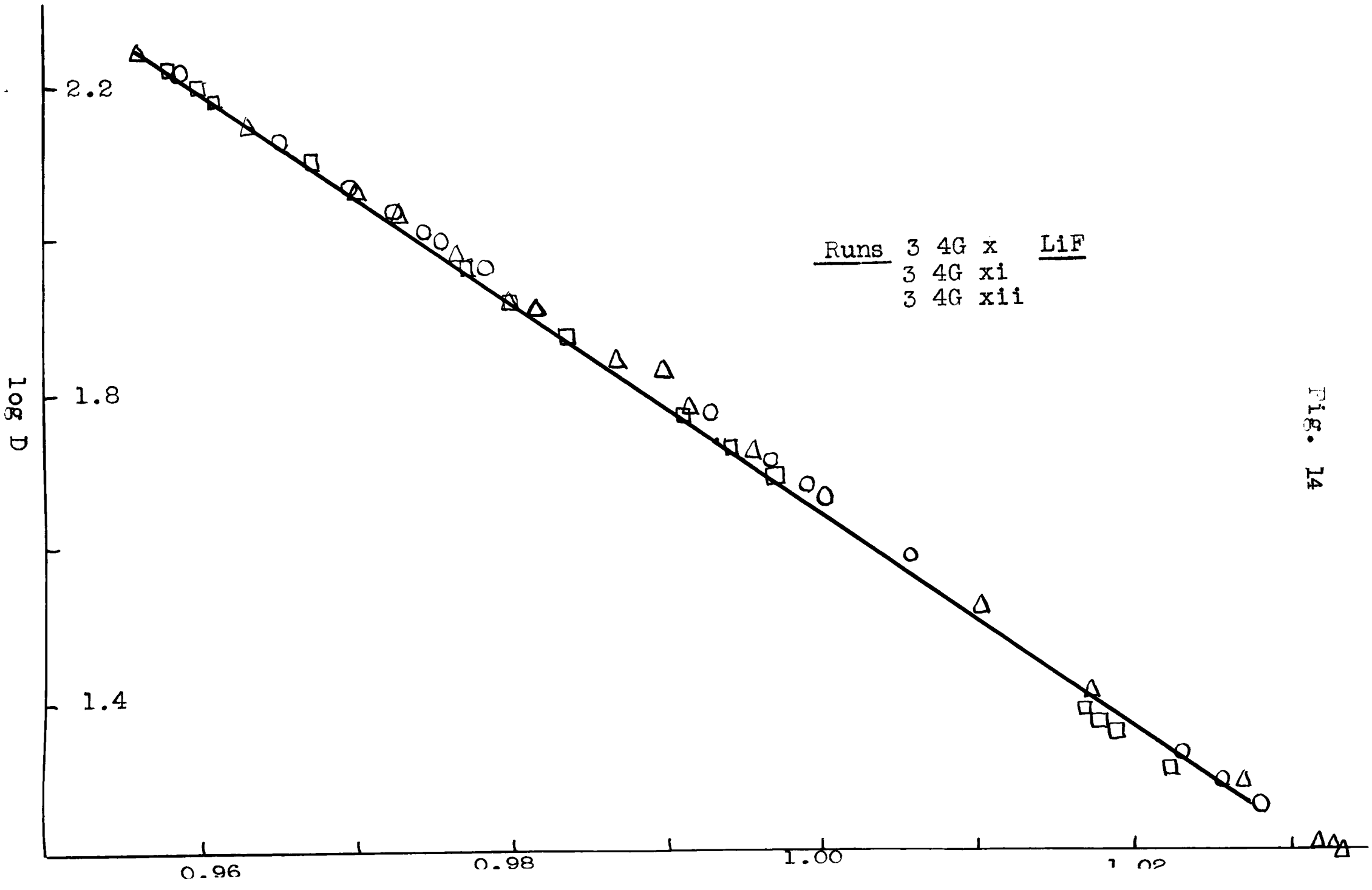
The experimental results are given in Tables XIV to XXXVIII. The headings of the columns are the same as those for the potassium chloride runs. The runs using the graphite cell are given first. These are much less reliable than those using the platinum vessel, and the following discussion applies only to the runs obtained using the latter vessel.

In Tables XXXIX to XLIII the results are collected and compared with those of other authors. The weighted mean of the second law values obtained with each vessel and the weighed mean third law values are also included.

The vapour pressure equation over the temperature range of the experiment for the platinum vessel only is given at the foot of each table. In Table XLIV the weighted mean second law values of the heat of sublimation found using the platinum vessel are tabulated with the mean third law values.

The following equations were used to convert the values of log D (where D is the deflection of the spot of light in centimetres) to log p(mm), allowance having been made for thermal expansion of the effusion holes.

	Platinum vessel	Graphite vessel
LiF	$\log p(mm) = \log D - 4.424$	$\log p(mm) = \log D - 4.739$
NaF	$\log p(mm) = \log D - 4.424$	$\log p(mm) = \log D - 4.740$
KF	$\log p(mm) = \log D - 4.423$	$\log p(mm) = \log D - 4.739$
RbF	$\log p(mm) = \log D - 4.421$	
CsF	$\log p(mm) = \log D - 4.420$	



Runs 3 4G x LiF
3 4G xi
3 4G xii

Fig. 14

TABLE XIV.

Run 3 4G (x1) LiF.

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.2433	1046.1	0.9559	5.7180	19.5150
2.2460	1046.1	0.9559	5.7207	19.5177
2.1452	1038.2	0.9632	5.6136	19.5159
2.0615	1030.6	0.9703	5.5242	19.5290
2.0362	1028.1	0.9727	5.4968	19.5363
1.9795	1024.0	0.9766	5.4367	19.5325
1.9112	1018.6	0.9817	5.3644	19.5338
1.8432	1013.2	0.9870	5.2917	19.5376
1.8351	1013.5	0.9867	5.3026	19.5441
1.8055	1010.2	0.9899	5.2516	19.5393
1.7767	1008.4	0.9917	5.2213	19.5350
1.7210	1004.2	0.9958	5.1623	19.5352
1.5159	989.7	1.0104	4.9456	19.5292
1.4099	982.8	1.0175	4.8339	19.5200
1.2945	973.7	1.0270	4.7110	19.5342
1.2122	969.1	1.0319	4.6241	19.5188
1.2068	968.4	1.0326	4.6191	19.5231
1.1987	967.9	1.0332	4.6105	19.5232

$$\Delta_g H_{298} = 65.14 \text{ Kcal/mole.}$$

95% confidence limit = 0.82 Kcal/mole.

TABLE XV.

Run 3 4G (xii) LiF.

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.2251	1043.7	0.9581	5.6977	20.0841
2.2209	1041.9	0.9598	5.6724	20.0843
2.1853	1040.6	0.9610	5.6559	20.0859
2.1031	1033.8	0.9673	5.5682	20.0928
1.9652	1023.4	0.9771	5.4218	20.0935
1.9191	1020.2	0.9802	5.3733	20.0916
1.8762	1016.5	0.9838	5.3276	20.0999
1.7701	1008.8	0.9913	5.2153	20.1002
1.7259	1005.6	0.9944	5.1686	20.1001
1.6830	1002.7	0.9973	5.1232	20.0982
1.3560	981.3	1.0191	4.7787	20.0811
1.3096	978.2	1.0223	4.7298	20.0802
1.1303	965.4	1.0358	4.5339	20.0930

$\Delta_s H_{298}$ = 67.81 Kcal/mole.

95% confidence limits = 0.88 Kcal/mole.

TABLE XVI.

Run 3 4G (xiii) LiF.

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.2428	1046.3	0.9557	5.7175	20.0042
2.1864	1040.8	0.9608	5.6571	20.0200
2.1504	1037.5	0.9639	5.6186	20.0279
1.7332	1005.7	0.9943	5.1759	20.0396
1.7076	1004.0	0.9960	5.1488	20.0379
1.6693	1001.2	0.9988	5.1081	20.0391
1.5011	989.8	1.0103	4.9306	20.0335
1.4983	990.1	1.0100	4.9282	20.0266
1.4564	987.4	1.0128	4.8842	20.0245
1.4031	984.1	1.0162	4.8281	20.0192
1.3444	980.2	1.0202	4.7662	20.0171
1.2480	973.7	1.0270	4.6646	20.0172
1.1847	969.3	1.0317	4.5976	20.0204
1.1239	965.6	1.0356	4.5336	20.0147

$\Delta_s H_{298}$ = 67.50 Kcal/mole.

95% confidence limit = 1.10 Kcal/mole.

TABLE XVII.

Run 3 4G (xiv) LiF.

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.2458	1045.6	0.9564	5.7203	20.3831
2.2052	1041.0	0.9606	5.6760	20.4032
2.1374	1036.3	0.9650	5.6043	20.2990
2.0095	1026.2	0.9745	5.4683	20.4086
1.9552	1022.0	0.9785	5.4109	20.4125
1.9148	1020.1	0.9803	5.3789	20.4081
1.8954	1017.6	0.9827	5.3477	20.4137
1.9031	1018.1	0.9822	5.3555	20.4139
1.8525	1014.7	0.9855	5.3024	20.4114
1.7760	1009.2	0.9909	5.2213	20.4131
1.6902	1003.2	0.9968	5.1306	20.4128
1.6304	999.2	1.0008	5.0678	20.4113
1.5933	996.6	1.0034	5.0286	20.4120
1.4099	984.7	1.0155	4.8354	20.4043
1.3674	982.3	1.0180	4.7910	20.3982
1.3324	979.2	1.0212	4.7535	20.4098
1.2923	977.0	1.0235	4.7116	20.4032
1.2529	974.3	1.0264	4.6700	20.4060
1.1903	920.8	1.0300	4.6045	20.3957
1.1644	969.0	1.0320	4.5771	20.3990

$\Delta_s H_{298}$ = 69.28 Kcal/mole.

95% confidence limits = 0.75 Kcal/mole.

Fig. 15

Runs on NaF using graphite vessel

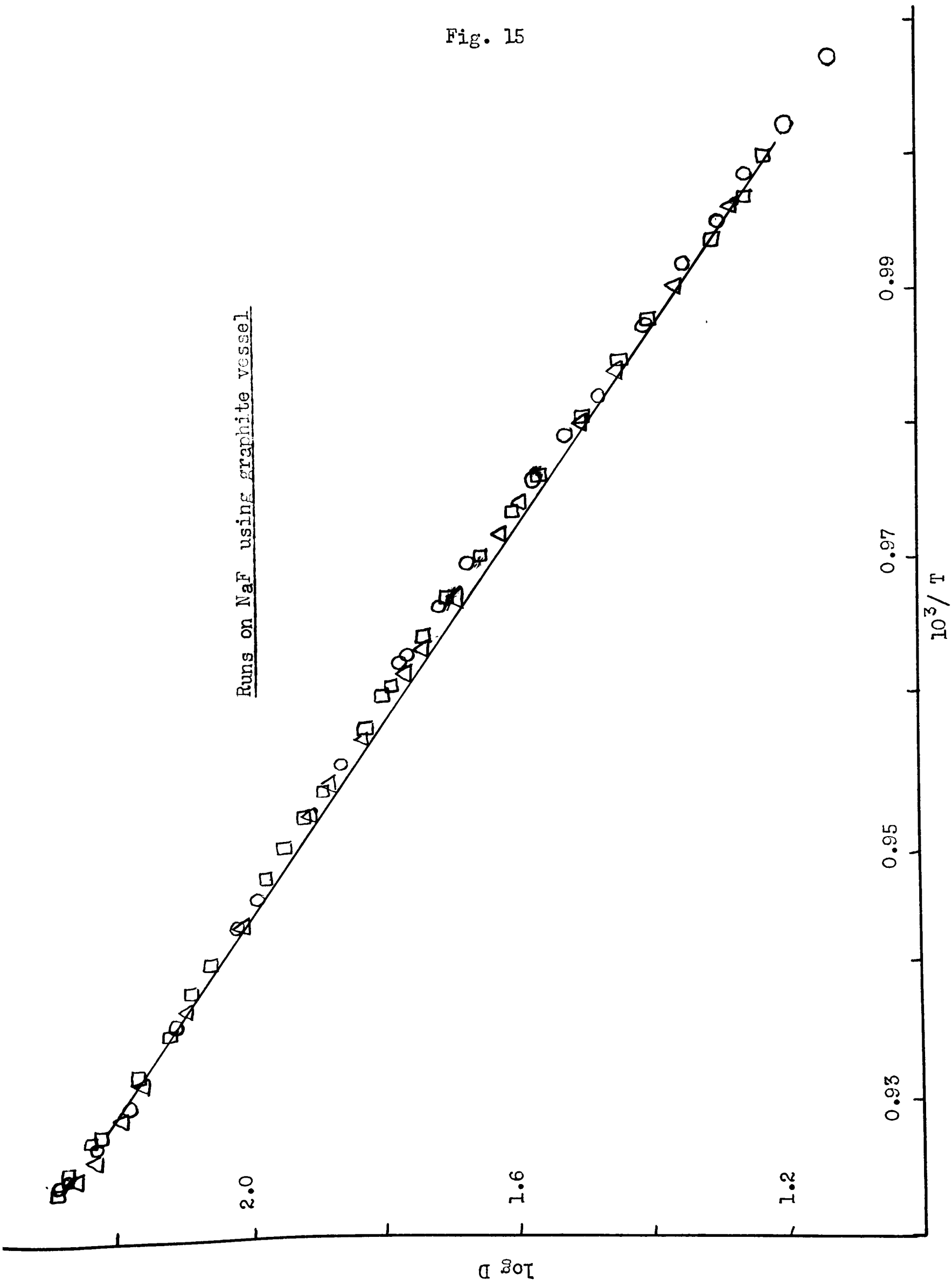


TABLE XVIII

Run 3 4G. XXV. NaF.

Log D	T	$\frac{10^3}{T}$		I"
2.2849	1082.1	0.9241	3.9531	17.3416
2.2711	1081.6	0.9246	3.9390	17.3348
2.2274	1078.3	0.9274	3.8931	17.3294
2.1790	1074.8	0.9304	3.8426	17.3224
2.1096	1068.6	0.9358	3.7693	17.3273
2.0245	1060.6	0.9429	3.6791	17.3400
1.9881	1057.7	0.9454	3.6410	17.3381
1.9217	1051.7	0.9508	3.5706	17.3460
1.8633	1047.0	0.9551	3.5093	17.3470
1.7686	1039.0	0.9625	3.4095	17.3544
1.7634	1038.0	0.9634	3.4037	17.3616
1.7101	1034.5	0.9667	3.3483	17.3540
1.6712	1031.0	0.9699	3.3070	17.3591
1.5717	1024.3	0.9763	3.2032	17.3480
1.5224	1020.9	0.9795	3.1518	17.3430
1.4742	1017.4	0.9829	3.1014	17.3418
1.3979	1012.3	0.9878	3.0218	17.5332
1.3385	1007.9	0.9922	2.9595	17.3347
1.2923	1004.5	0.9955	2.9114	17.3344
1.2355	1001.1	0.9989	2.8522	17.3244
1.1903	997.4	1.0026	2.8047	17.3306
1.1271	992.7	1.0074	2.7384	17.3338

ΔH_{298} = 66.09 Kcal/mole.

95% confidence limit = 0.86 Kcal/mole.

TABLE XIX.

Run 3 4G XXVII NaF.

Log_{e} D	T	$\frac{10^3}{T}$	Σ	I"
2.2648	1081.6	0.9246	3.9327	15.2090
2.2294	1079.1	0.9267	3.8956	15.2020
2.1901	1076.1	0.9293	3.8544	15.1982
2.1652	1073.8	0.9313	3.8282	15.2007
2.0945	1067.6	0.9367	3.7536	15.2036
2.0183	1060.6	0.9429	3.6729	15.2119
1.9112	1051.4	.9511	3.5599	15.2167
1.8820	1048.9	0.9534	3.5292	15.2190
1.8299	1045.0	0.9569	3.4746	15.2147
1.7657	1039.8	0.9617	3.4072	15.2162
1.7404	1037.9	0.9635	3.3806	15.2154
1.6875	1033.9	.9672	3.3252	15.2132
1.6201	1028.7	0.9721	3.2545	15.2128
1.5888	1026.2	0.9745	3.2216	15.2144
1.4997	1020.2	0.9802	3.1285	15.2031
1.4456	1015.9	0.9843	3.0718	15.2053
1.3541	1009.6	0.9905	2.9763	15.1988
1.2742	1003.7	.9963	2.8927	15.1985

$\Delta_s H_{298}$ = 65.50 Kcal/mole.

95% confidence limit = 0.86 Kcal/mole.

TABLE XX.

Run 3 4G XXVIII. NaF.

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.2903	1082.6	0.9237	3.9586	17.5338
2.2695	1081.1	0.9250	3.9370	17.5313
2.2375	1078.4	0.9273	3.9032	17.5313
2.2271	1077.9	0.9277	3.8926	17.5266
2.1706	1072.9	0.9321	3.8330	17.5317
2.1255	1069.1	0.9354	3.7057	17.5329
2.0931	1065.9	0.9382	3.7511	17.5394
2.0630	1063.3	0.9405	3.7192	17.5413
1.9811	1056.3	0.9467	3.6330	17.5462
1.9523	1053.9	0.9489	3.6026	17.5482
1.9186	1051.4	0.9511	3.5673	17.5452
1.8274	1044.4	0.9575	3.4716	17.5436
1.7980	1041.8	0.9599	3.4408	17.5480
1.8993	1049.2	0.9531	3.5465	17.5538
1.8122	1043.0	0.9588	3.4557	17.5468
1.7896	1040.8	0.9608	3.4318	17.5523
1.7396	1036.9	0.9644	3.3791	17.5525
1.6981	1033.9	0.9672	3.3358	17.5503
1.6503	1030.5	0.9704	3.2859	17.5474
1.6021	1027.0	0.9737	3.2355	17.5455
1.5635	1024.3	0.9763	3.1950	17.5432
1.5011	1019.6	0.9808	3.1297	17.5441
1.4440	1015.3	0.9849	3.0698	17.5449
1.3945	1012.3	0.9878	3.0184	17.5357
1.3010	1006.1	0.9939	2.9209	17.5278
1.2504	1002.7	0.9973	2.8682	17.5251
1.2095	1000.1	0.9999	2.8256	17.5207

ΔH_{298} = 67.05 Kcal/mole.

95% confidence limit = 0.76 Kcal/mole.

Fig. 16

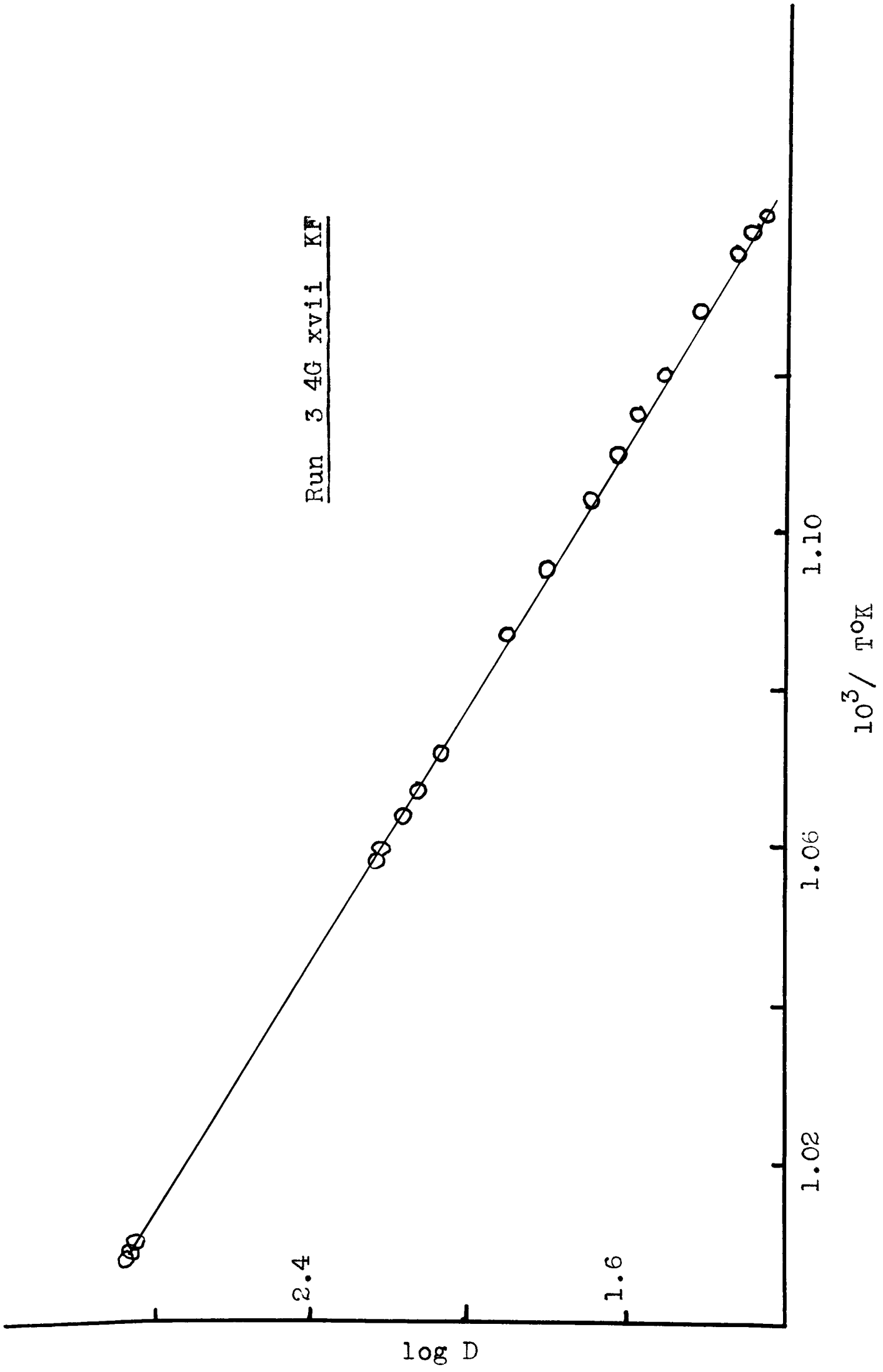


TABLE XXI.

Run 3 4G (xv) KF.

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.2312	943.6	1.0598	5.7619	19.3791
2.1864	940.3	1.0635	5.7142	19.3789
2.1467	937.0	1.0672	5.6719	19.3841
2.1239	935.3	1.0692	5.6477	19.3856
2.1169	934.8	1.0697	5.6402	19.3846
2.0821	932.1	1.0728	5.6033	19.3876
2.0366	928.8	1.0767	5.5550	19.3893
1.9800	924.5	1.0817	5.4949	19.3935
1.9571	922.6	1.0839	5.4703	19.3971
1.8797	917.7	1.0897	5.3888	19.3901
1.8681	916.7	1.0909	5.3763	19.3931
1.7604	909.4	1.0996	5.2625	19.3910
1.6637	902.8	1.1077	5.1614	19.3940
1.6201	899.9	1.1112	5.1143	19.3919
1.5809	897.5	1.1142	5.0730	19.3891
1.4967	892.1	1.1210	4.9842	19.3905
1.4472	889.2	1.1246	4.9323	19.3821
1.4065	886.1	1.1285	4.8889	19.3888
1.2455	876.8	1.1405	4.7199	19.3740

$\Delta_s H_{298}$ = 58.16 Kcal/mole.

95% confidence limits = 0.57 Kcal.

Run 3 4G (xvi) KF.

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.2440	944.6	1.0586	5.7755	19.2828
2.2338	943.9	1.0594	5.7647	19.2822
2.1973	941.3	1.0624	5.7260	19.2818
2.1697	938.9	1.0651	5.6965	19.2867
2.0962	933.7	1.0710	5.6187	19.2842
2.0667	930.5	1.0747	5.5865	19.3037
1.8531	916.3	1.0917	5.3609	19.2905
1.7903	911.6	1.0970	5.2943	19.2915
1.7308	907.5	1.1019	5.2314	19.2912
1.6684	903.3	1.1071	5.1654	19.2915
1.4472	889.0	1.1249	4.9321	19.2853
1.3997	885.9	1.1288	4.8818	19.2848
1.2833	878.3	1.1386	4.7590	19.2870
1.2504	876.6	1.1408	4.7247	19.2808

$\Delta_g H_{298}$ = 57.75 Kcal/mole.

95% confidence limits = 0.48 Kcal.

TABLE XXIII.

Run 3 40 (xvii) KF.

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.2438	944.9	1.0583	5.7755	19.3713
2.2348	944.1	1.0592	5.7659	19.3733
2.1807	940.1	1.0637	5.7089	19.3741
2.1424	937.2	1.0670	5.6677	19.3753
2.0824	932.6	1.0723	5.6040	19.3797
1.9085	919.5	1.0875	5.4191	19.3900
1.9063	919.5	1.0875	5.4169	19.3878
1.8102	912.9	1.0954	5.3153	19.3877
1.6998	905.4	1.1045	5.1986	19.3861
1.6294	900.6	1.1104	5.1241	19.3892
1.5763	897.1	1.1147	5.0680	19.3884
1.5079	892.6	1.1203	4.9959	19.3882
1.4133	886.4	1.1282	4.8960	19.3898
1.3324	881.4	1.1346	4.8108	19.3868
1.2923	878.8	1.1379	4.7685	19.3869
1.2625	876.9	1.1404	4.7370	19.3875
2.8677	992.1	1.0080	6.4377	19.3873
2.8597	991.1	1.0090	6.4290	19.3915
2.8497	989.9	1.0102	6.4176	19.3955
2.8701	992.1	1.0080	6.4401	19.3897
2.8705	992.1	1.0080	6.4405	19.3901

$\Delta_g H_{298}$ = 58.15 Kcal/mole.

95% confidence limits = 0.31 Kcal/mole.

Fig. 17

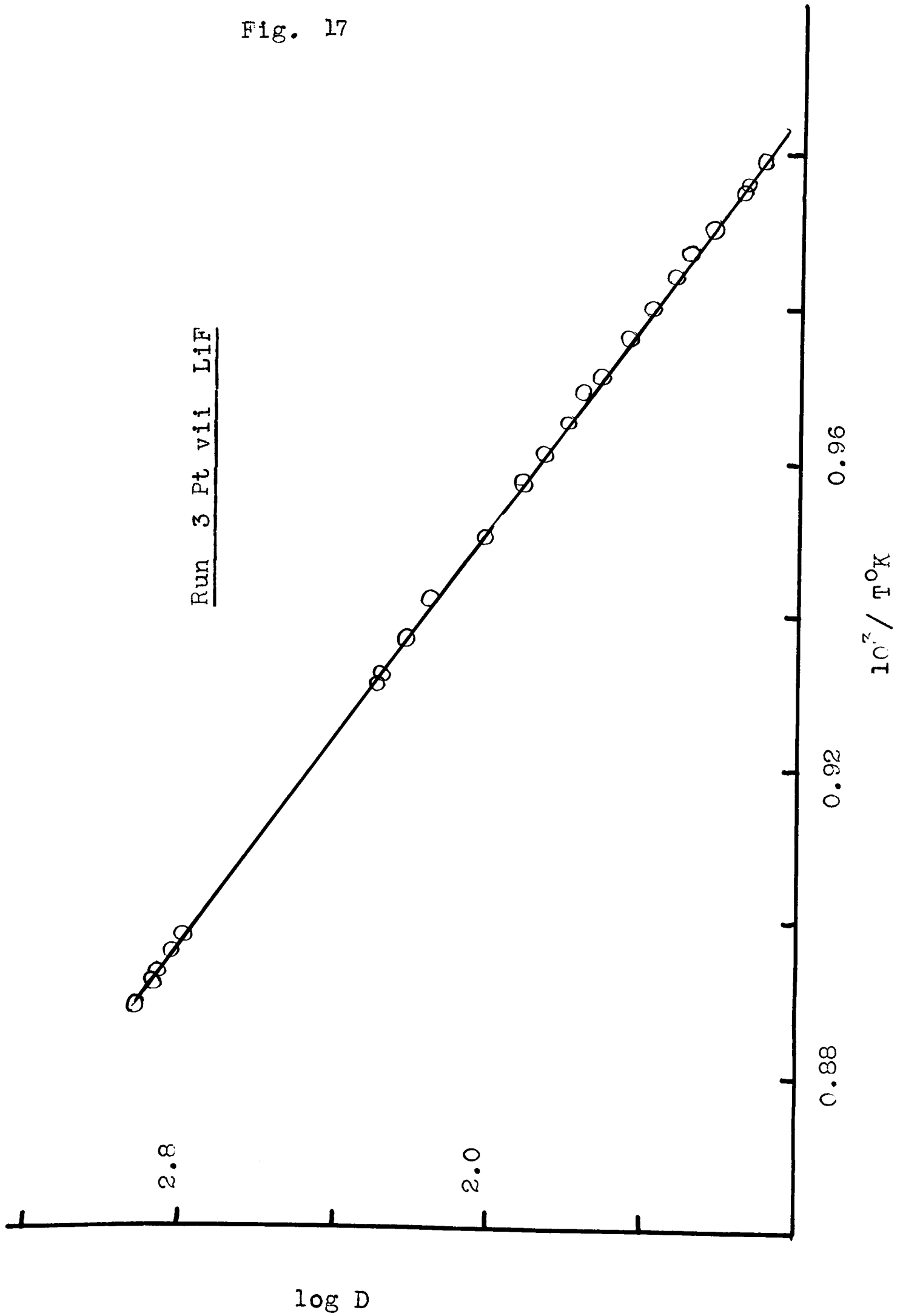


TABLE XXIV.

Run 3Pt (#11) LiF.

Log D	T	Σ	$\frac{10^3}{T}$	I"
2.9222	1124.6	6.4578	0.8892	20.3931
2.9180	1124.4	6.4330	0.8894	20.3915
2.8745	1120.4	6.4064	0.8925	20.3934
2.8691	1119.6	6.4008	0.8932	20.3988
2.8276	1116.1	6.3564	0.8960	20.3983
2.8229	1115.6	6.3516	0.8964	20.3998
2.7996	1113.4	6.3262	0.8981	20.4010
2.3012	1073.8	5.7976	0.9313	20.3927
2.2907	1072.8	5.7863	0.9321	20.4096
2.2256	1067.6	5.7174	0.9367	20.3971
2.1562	1061.7	5.6432	0.9419	20.4044
2.0245	1052.2	5.5039	0.9504	20.3983
1.9186	1044.5	5.3923	0.9574	20.3964
1.8681	1040.9	5.3388	0.9607	20.3947
1.8136	1036.6	5.2810	0.9647	20.3995
1.7657	1033.2	5.2307	0.9679	20.3994
1.7210	1029.7	5.1829	0.9712	20.4033
1.6532	1024.7	5.1111	0.9759	20.4052
1.5877	1020.2	5.0419	0.9801	20.4018
1.5315	1016.7	4.9831	0.9836	20.3978
1.4857	1013.5	4.9347	0.9867	20.3980
1.4298	1009.8	4.8757	0.9903	20.3954
1.3541	1004.7	4.7960	0.9953	20.3941
1.3424	1004.2	4.7836	0.9958	20.3895
1.3012	1001.5	4.7406	0.9985	20.3889

$\Delta_s H_{298}$ = 70.81 Kcal/mole.

95% confidence limits = 0.44 Kcal/mole.

TABLE XXV.

Run 3Pt (viii) LiF.

Log D	T	Σ	$\frac{10^3}{T}$	I''
2.9190	1125.6	6.4553	0.8884	20.2729
2.9075	1123.6	6.4423	0.8900	20.2848
2.8983	1122.1	6.4316	0.8912	20.2927
2.8846	1121.9	6.4179	0.8913	20.2806
2.8525	1119.1	6.3836	0.9836	20.2820
2.8247	1116.5	6.3541	0.8957	20.2852
2.7994	1114.3	6.3267	0.8974	20.2842
2.2487	1069.6	5.7420	0.9349	20.2828
2.2098	1066.6	5.7009	0.9376	20.2837
2.1553	1062.6	5.6431	0.9411	20.2803
2.1096	1059.2	5.5946	0.9441	20.2785
1.9912	1050.4	5.4691	0.9520	20.2759
1.9269	1045.8	5.4015	0.9562	20.2736
1.8739	1041.5	5.3453	0.9602	20.2796
1.8089	1036.9	5.2763	0.9644	20.2759
1.7582	1033.9	5.2233	0.9672	20.2665
1.6503	1024.9	5.1082	0.9757	20.2836
1.6274	1023.3	5.0840	0.9772	20.2827
1.5717	1019.2	5.0251	0.9812	20.2860
1.5024	1014.5	5.9523	0.9857	20.2832
1.4265	1009.0	5.8717	0.9911	20.2865
1.3502	1003.7	5.7913	0.9963	20.2871
1.3201	1001.6	5.7596	0.9984	20.2880

$\Delta_g H_{298}$ = 70.27 Kcal/mole.

95% confidence limits = 0.31 Kcal/mole.

TABLE XXVI.

Run 3Pt (ix) LiF.

Log D	T	Σ	$\frac{10^3}{T}$	I"
2.9044	1123.1	6.4386	0.8904	20.3000
2.8948	1123.1	6.4289	0.8904	20.2903
2.8434	1118.6	6.3741	0.8940	20.2915
2.8252	1117.0	6.3547	0.8955	20.2924
2.8022	1115.1	6.3302	0.8968	20.2912
2.6737	1071.8	5.7686	0.9330	20.2932
2.2076	1066.8	5.6987	0.9374	20.2918
2.1581	1062.8	5.6459	0.9409	20.2935
2.0770	1056.9	5.5603	0.9462	20.2904
2.0183	1051.9	5.4976	0.9507	20.2977
1.9238	1045.5	5.3983	0.9565	20.2887
1.7952	1035.7	5.2619	0.9655	20.2924
1.7267	1030.5	5.1894	0.9704	20.2962
1.6590	1025.6	5.1182	0.9750	20.2966
1.5966	1021.2	5.0515	0.9792	20.2953
1.5024	1014.5	4.9523	0.9857	20.2973
1.4014	1008.0	4.8459	0.9921	20.2905
1.3856	1006.5	4.8291	0.9935	20.2955
1.3201	1002.6	4.7603	0.9974	20.2874
1.3096	1001.6	4.7491	0.9984	20.2918

$\Delta_s H_{298}$ = 70.33 Kcal/mole.

95% confidence limit = 0.29 Kcal/mole.

Fig. 18

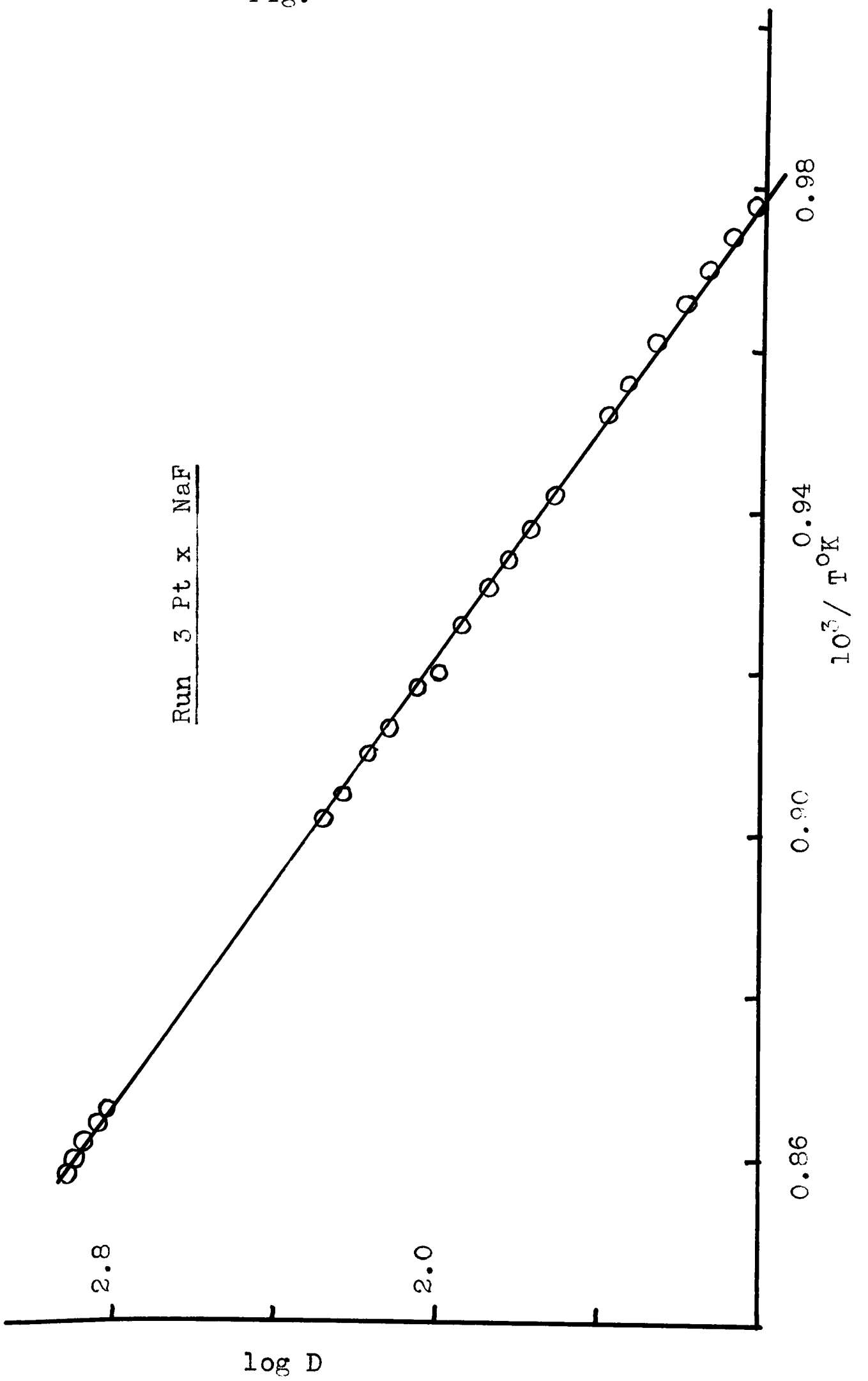


TABLE XXVII.

Run 3Pt (x) NaF.

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.9249	1165.0	0.8584	4.6449	17.5318
2.9014	1162.2	0.8604	4.6198	17.5367
2.8783	1160.2	0.8619	4.5955	17.5349
2.8418	1156.9	0.8644	4.5568	17.5338
2.8190	1154.5	0.8662	4.5325	17.5365
2.2916	1109.0	0.9017	3.9767	17.5136
2.2425	1104.5	0.9054	3.9248	17.5173
2.1841	1099.5	0.9095	3.8632	17.5192
2.1323	1095.2	0.9131	3.8087	17.5168
2.0550	1088.9	0.9184	3.7275	17.5152
2.0052	1084.6	0.9220	3.6750	17.5167
1.9479	1079.8	0.9261	3.6146	17.5179
1.8842	1074.6	0.9306	3.5477	17.5185
1.8370	1070.3	0.9343	3.4978	17.5242
1.7839	1066.6	0.9376	3.4423	17.5182
1.7251	1061.7	0.9419	3.3804	17.5209
1.5877	1050.7	0.9517	3.2361	17.5237
1.5366	1046.4	0.9556	3.1822	17.5283
1.4698	1041.0	0.9606	3.1121	17.5333
1.3979	1035.6	0.9656	3.0368	17.5331
1.3404	1031.0	0.9699.	2.9763	17.5371
1.2810	1027.0	0.9737	2.9144	17.5323
1.2330	1022.8	0.9777	2.8636	17.5415

$\Delta_s H_{298}$ = 68.49 Kcal/mole.

95% confidence limit = 0.47 Kcal/mole.

TABLE XXVIII.

Run 3Pt (xi) NaF.

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.9063	1163.5	0.8595	4.6254	17.6194
2.9068	1163.5	0.8595	4.6260	17.6200
2.8720	1160.2	0.8619	4.5892	17.6195
2.8246	1155.8	0.8652	4.5389	17.6191
2.7979	1152.8	0.8675	4.5103	17.6253
2.2718	1107.9	0.9026	3.9563	17.6019
2.1523	1097.8	0.9109	3.8304	17.6015
2.1014	1093.4	0.9146	3.7766	17.6036
2.0366	1088.2	0.9189	3.7087	17.6007
1.9643	1081.3	0.9248	3.6320	17.6132
1.8848	1075.3	0.9300	3.5487	17.6085
1.8149	1069.8	0.9348	3.4753	17.6077
1.7348	1063.3	0.9405	3.3911	17.6097
1.7267	1062.6	0.9411	3.3826	17.6103
1.6599	1057.2	0.9459	3.3124	17.6126
1.5798	1050.9	0.9516	3.2283	17.6147
1.5289	1046.8	0.9553	3.1748	17.6171
1.4249	1038.8	0.9626	3.0658	17.6185
1.4314	1039.0	0.9625	3.0724	17.6236
1.3541	1033.2	0.9679	2.9914	17.6242
1.2878	1028.2	0.9726	2.9220	17.6259

$\Delta_s H_{298}$ = 68.98 Kcal/mole.

95% confidence limit = 0.46 Kcal/mole.

TABLE XXIX.

Run 3Pt (xii) NaF.

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.9264	1165.8	0.8578	4.6469	17.6687
2.8936	1162.3	0.8604	4.6120	17.6733
2.8627	1159.7	0.8623	4.5795	17.6696
2.8389	1157.4	0.8640	4.5542	17.6701
2.8083	1154.6	0.8661	4.5220	17.6698
2.2949	1110.0	0.9009	3.9807	17.6568
2.2271	1104.2	0.9056	3.9091	17.6565
2.1703	1099.6	0.9096	3.8494	17.6575
2.1113	1094.4	0.9137	3.7872	17.6376
2.0141	1086.7	0.9202	3.6851	17.6541
1.9494	1082.2	0.9240	3.6177	17.6444
1.8109	1069.8	0.9348	3.4713	17.6620
1.7177	1062.3	0.9414	3.3734	17.6643
1.6325	1055.7	0.9472	3.2841	17.6630
1.5670	1050.5	0.9519	3.2152	17.6655
1.4983	1045.3	0.9567	3.1433	17.6664
1.4031	1037.4	0.9639	3.0431	17.6755
1.3385	1032.5	0.9685	2.9754	17.6777
1.2648	1027.7	0.9730	2.8986	17.6692

$\Delta_s H_{298}$ = 69.26 Kcal/mole.

95% confidence limits = 0.49 Kcal/mole.

Fig. 19

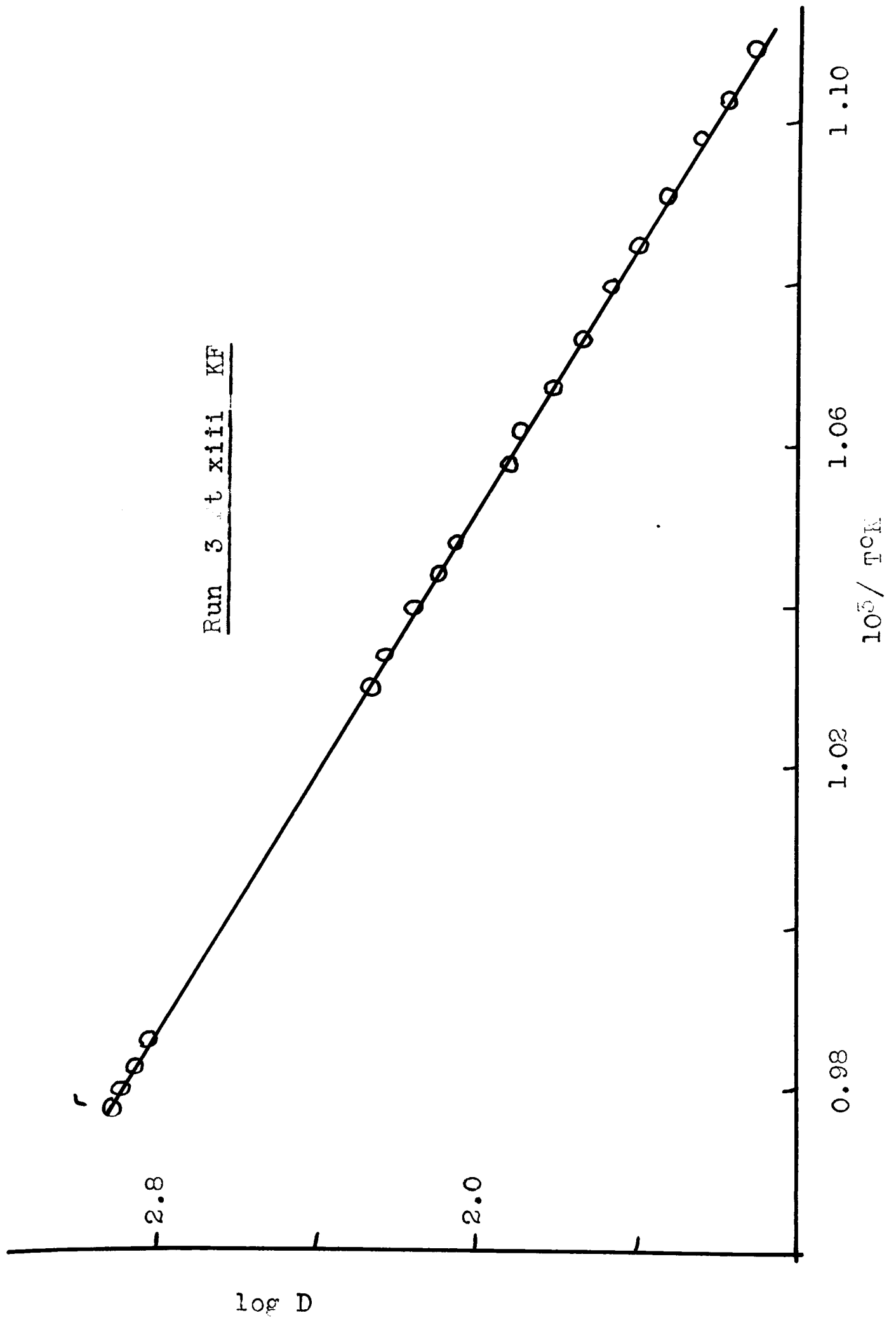


TABLE XXX.

Run 3Pt (xiii) KF.

Log D	T	Σ	$\frac{10^3}{T}$	I"
2.9222	1023.2	6.5171	0.9773	19.2759
2.9254	1022.9	6.5201	0.9776	19.2828
2.8943	1020.3	6.4869	0.9801	19.2823
2.8568	1017.3	6.4470	0.9830	19.2802
2.8253	1014.6	6.4134	0.9856	19.8528
2.2735	970.7	5.8263	1.0302	19.2757
2.2175	966.7	5.7672	1.0344	19.2715
2.1553	961.9	5.7009	1.0396	19.2731
2.0948	957.4	5.6368	1.0445	19.2729
2.0565	954.6	5.5961	1.0476	19.2727
1.9227	945.0	5.4545	1.0882	19.2695
1.8871	941.9	5.4163	1.0617	19.2770
1.8149	936.9	5.3400	1.0674	19.2751
1.7412	931.5	5.2618	1.0735	19.2765
1.6675	926.2	5.1837	1.0797	19.2794
1.5955	921.5	5.1079	1.0852	19.2754
1.5263	916.8	5.0347	1.0908	19.2753
1.4502	911.2	4.9539	1.0975	19.2820
1.3838	906.5	4.8835	1.1031	19.2847
1.3075	901.5	4.8028	1.1093	19.2849

$\Delta_s H_{298}$ = 59.11 Kcal/mole.

95% confidence limits = 0.22 Kcal/mole.

TABLE XXXI.

Run 3Pt (xiv) FF.

Log D	T	Σ	$\frac{10^3}{T}$	I"
2.9111	1021.8	6.5049	0.9798	19.2050
2.8763	1018.8	6.4676	0.9815	19.2040
2.8408	1015.8	6.4298	0.9844	19.2038
2.8105	1013.4	6.3976	0.9868	19.2028
2.2889	971.8	5.8425	1.0290	19.1953
2.2567	969.4	5.8086	1.0316	19.1951
1.9827	948.8	5.5176	1.0540	19.1948
1.9238	944.6	5.4553	1.0586	19.1922
1.8142	936.3	5.3388	1.0680	19.1977
1.7364	930.7	5.2564	1.0745	19.1996
1.6551	924.6	5.1700	1.0815	19.2041
1.5809	919.8	5.0918	1.0872	19.1998
1.5119	914.8	5.0184	1.0931	19.2030
1.4362	909.6	4.9385	1.0994	19.2048
1.3766	905.3	4.8752	1.1046	19.2090

$\Delta_s H_{298}$ = 58.74 Kcal/mole.

95% confidence limit = 0.29 Kcal/mole.

TABLE XXXII.

Run 3Pt (xv) KF.

Log D	T	Σ	$\frac{10^3}{T}$	I"
2.9274	1023.2	6.5223	0.9773	19.2582
2.8923	1020.2	6.4848	0.9802	19.2585
2.8582	1017.2	6.4484	0.9831	19.2599
2.8322	1015.1	6.4207	0.9851	19.2583
2.7979	1012.4	6.3843	0.9877	19.2558
2.2380	968.2	5.7889	1.0328	19.2481
2.2151	966.5	5.7647	1.0347	19.2486
2.1129	958.9	5.6562	1.0429	19.2470
2.0366	953.2	5.5752	1.0491	19.2468
1.9533	946.7	5.4866	1.0563	19.2521
1.8698	940.8	5.3982	1.0629	19.2497
1.8041	935.8	5.3283	1.0686	19.2540
1.7235	930.0	5.2430	1.0753	19.2561
1.6415	924.6	5.1564	1.0815	19.2503
1.6042	921.5	5.1166	1.0852	19.2587
1.5416	917.5	5.0505	1.0899	19.2538
1.3729	905.3	4.8715	1.1046	19.2664
1.3181	902.0	4.8140	1.1086	19.2610

$\Delta_s H_{298}$ = 59.00 Kcal/mole.

95% confidence limits = 0.30 Kcal/mole.

Fig. 20

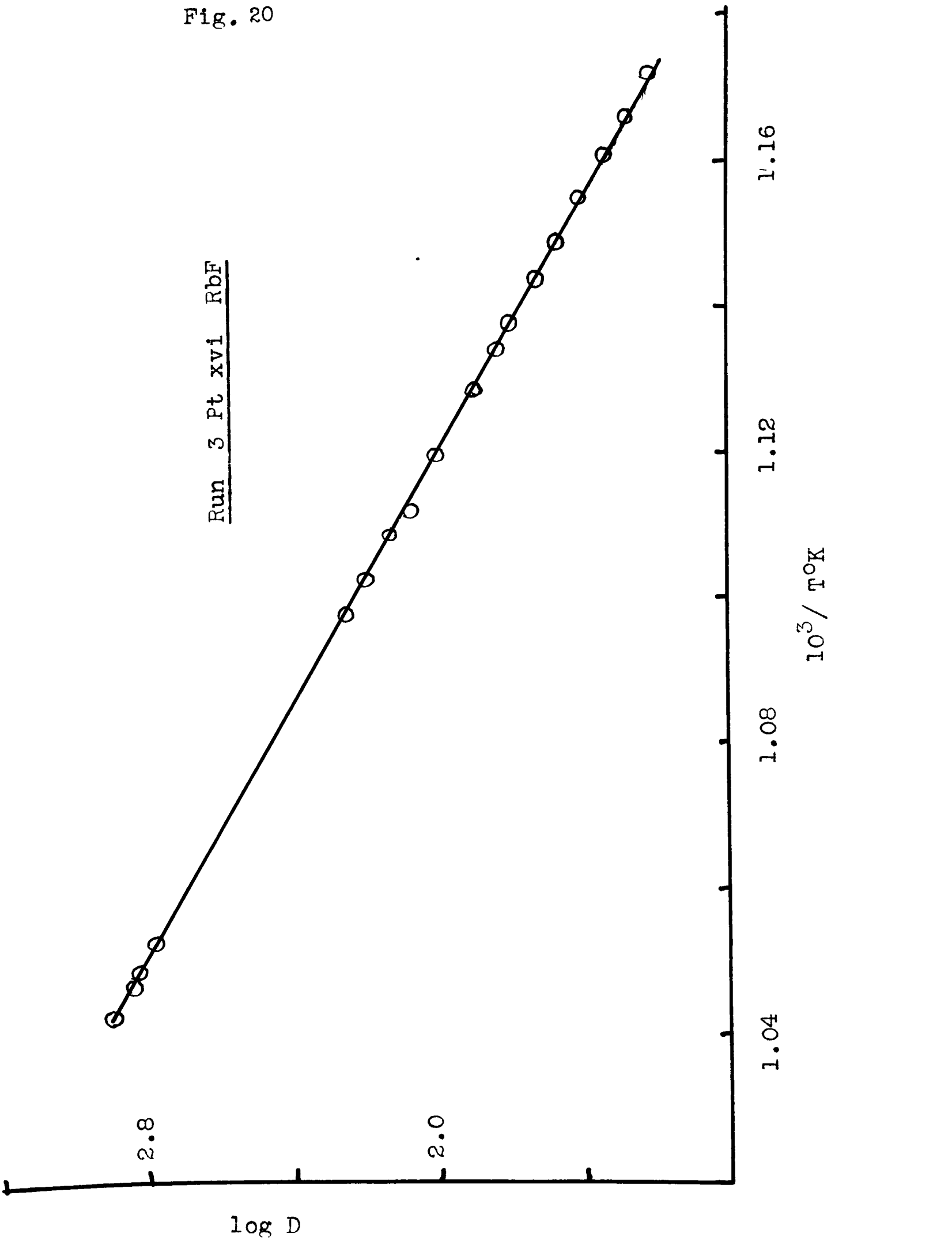


TABLE XXXIII.

Run 3Pt XVI. RbF.

Log D	T	Σ	$\frac{10^3}{T}$	I"
2.9045	958.6	7.6752	1.0432	20.5508
2.8549	955.1	7.6217	1.0470	20.5442
2.8365	953.2	7.6022	1.0491	20.5507
2.7889	949.6	7.5513	1.0531	20.5491
2.2563	910.5	6.9811	1.0983	20.5368
2.1998	906.5	6.9188	1.1031	20.5337
2.1380	902.0	6.8486	1.1086	20.5314
2.0763	898.0	6.7891	1.1136	20.5330
2.0086	893.2	6.7168	1.1196	20.5354
1.9047	885.7	6.6053	1.1291	20.5411
1.8376	881.4	6.5341	1.1346	20.5378
1.8089	878.8	6.5028	1.1379	20.5473
1.7284	873.8	6.4172	1.1444	20.5419
1.6702	870.0	6.3552	1.1494	20.5416
1.6085	865.5	6.2891	1.1554	20.5496
1.5453	861.5	6.2219	1.1608	20.5490
1.4771	857.3	6.1495	1.1664	20.5457
1.4183	853.0	6.0861	1.1723	20.5551

$\Delta_s H_{298}$ = 55.62 Kcal/mole.

95% confidence limits = 0.25 Kcal/mole.

TABLE XXXIV.

Run 3Pt. XVII. RbF.

Log D	T	Σ	$\frac{10^3}{T}$	I"
2.9169	959.8	7.6888	1.0419	20.4774
2.8607	955.6	7.6287	1.0465	20.4738
2.8341	953.2	7.5998	1.0491	20.4768
2.7918	950.1	7.5545	1.0525	20.4732
2.2936	913.4	7.0215	1.0948	20.4595
2.2191	908.1	6.9417	1.1012	20.4582
2.1467	902.9	6.8642	1.1075	20.4580
2.0569	896.6	6.7683	1.1153	20.4579
1.9965	892.3	6.7037	1.1207	20.4596
1.9232	887.3	6.6254	1.1270	20.4586
1.8585	882.6	6.5562	1.1330	20.4630
1.6513	868.4	6.3347	1.1515	20.4686
1.5763	863.4	6.2546	1.1582	20.4707
1.5289	859.6	6.2036	1.1633	20.4823
1.4728	856.1	6.1440	1.1681	20.4817
1.4265	853.?	6.0951	1.1714	20.4733

$\Delta_s H_{298}$ = 55.31 Kcal/mole.

95% confidence limit = 0.52 Kcal/mole.

TABLE XXXV.

Run 3Pt (xviii) RbF.

Log D	T	Σ	$\frac{10^3}{T}$	I"
2.9110	959.1	7.6821	1.0426	20.5929
2.8644	955.8	7.6325	1.0462	20.5879
2.8359	953.2	7.6016	1.0491	20.5929
2.8050	950.7	7.5683	1.0519	20.5943
2.2253	908.4	6.9483	1.1008	20.5799
2.1801	904.8	6.8995	1.1052	20.5855
2.0810	897.7	6.7934	1.1140	20.5884
2.0124	892.0	6.7194	1.1211	20.6023
1.9370	888.0	6.6399	1.1261	20.5848
1.8525	881.9	6.5494	1.1339	20.5909
1.7952	877.6	6.4879	1.1395	20.5987
1.6395	867.9	6.3225	1.1522	20.5906
1.5211	860.3	6.1965	1.1624	20.5909
1.4639	856.8	6.1357	1.1671	20.5883
1.4150	853.5	6.0835	1.1716	20.5918

$\Delta_s H_{298}$ = 55.81 Kcal/mole.

95% confidence limits = 0.33 Kcal/mole.

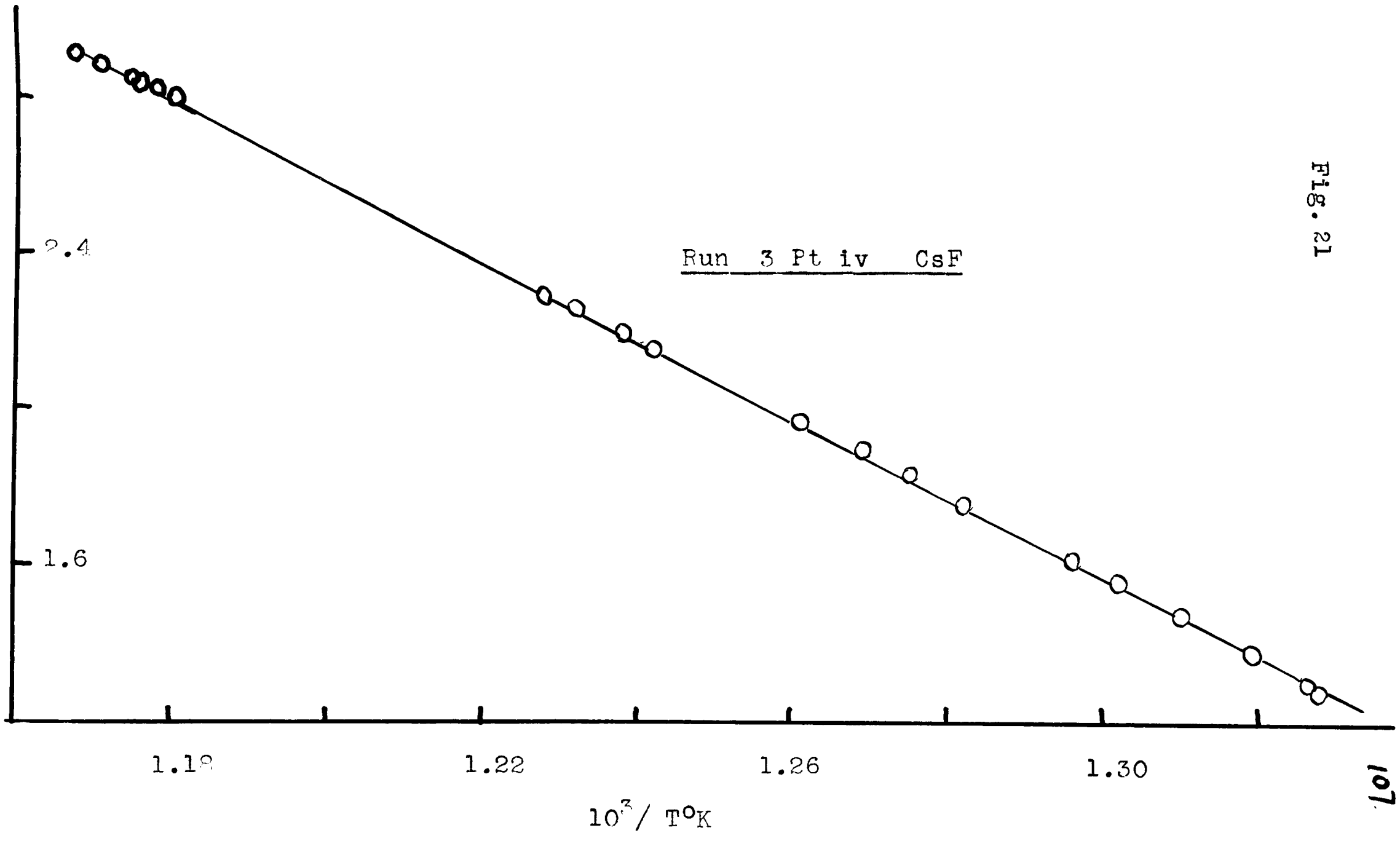


Fig. 21

TABLE XXXVI.

Run 3Pt IV CsF

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.9245	855.9	1.1684	6.7319	19.4427
2.8984	853.8	1.1712	6.7040	19.4453
2.8998	854.0	1.1710	6.7056	19.4447
2.8607	850.9	1.1752	6.6637	19.4485
2.8501	850.2	1.1762	6.6524	19.4480
2.8315	849.0	1.1778	6.6327	19.4458
2.8104	847.1	1.1805	6.6100	19.4524
2.3047	814.1	1.2284	6.0741	19.4376
2.3065	814.1	1.2284	6.0759	19.4394
2.2660	811.7	1.2320	6.0332	19.4359
2.2076	807.7	1.2381	5.9711	19.4401
2.1649	804.9	1.2424	5.9258	19.4416
1.9773	792.8	1.2614	5.7268	19.4493
1.9058	788.3	1.2686	5.6510	19.4518
1.8445	784.5	1.2747	5.5861	19.4433
1.7566	779.4	1.2830	5.4933	19.4508
1.6201	771.6	1.2960	5.3496	19.4485
1.5575	768.0	1.3021	5.2833	19.4486
1.4713	763.3	1.3101	5.1926	19.4449
1.3784	758.2	1.3189	5.0949	19.4430
1.2989	753.9	1.3264	5.0111	19.4407
1.2878	753.2	1.3277	4.9992	19.4430

Δ_{sH} 298 = 49.073 Kcal.

95% confidence limit = 0.18 Kcal/mole.

TABLE XXXVII

Run 3Ptv CsF

Log D	T	$\frac{10^3}{T}$	Σ	I"
2.9167	855.1	1.1695	6.7234	19.3013
2.8819	852.5	1.1730	6.6862	19.3017
2.8567	850.4	1.1759	6.6591	19.3008
2.8242	848.3	1.1788	6.6248	19.3027
2.2969	813.3	1.2296	6.0656	19.2899
2.2700	811.4	1.2324	6.0368	19.2912
2.0748	798.4	1.2525	5.8295	19.3001
2.0484	796.8	1.2550	5.8017	19.2991
1.9886	793.2	1.2607	5.7385	19.2972
1.9768	792.5	1.2618	5.7260	19.2966
1.9274	789.4	1.2668	5.6737	19.2981
1.8756	785.6	1.2729	5.6183	19.3083
1.7143	776.3	1.2882	5.4481	19.3026
1.6571	772.6	1.2943	5.3875	19.3076
1.4440	760.7	1.3146	5.1629	19.3013
1.4166	759.3	1.3170	5.1341	19.2984

$\Delta_S H_{298}$ = 48.51 Kcal/mole.

95% confidence limit = 0.26 Kcal/mole.

TABLE XXXVIII

Run 3Pt VI. CsF.

Log D	T	$\frac{10^3}{T}$	$\sum$	I"
2.8950	853.7	1.1714	6.7005	19.3085
2.8670	851.6	1.1743	6.6705	19.2094
2.8290	849.0	1.1779	6.6302	19.2076
2.8021	846.6	1.1812	6.6012	19.2138
2.2778	812.4	1.2309	6.0457	19.1890
2.2648	811.0	1.2330	6.0313	19.1970
2.2312	808.8	1.2364	5.9959	19.1979
2.1796	805.3	1.2418	5.9409	19.2006
2.1281	801.7	1.2473	5.8858	19.2042
2.0674	798.2	1.2528	5.8192	19.1963
1.9112	788.3	1.2686	5.6564	19.2022
1.8585	785.2	1.2736	5.6008	19.2000
1.7694	780.0	1.2821	5.5067	19.1967
1.7101	776.3	1.2882	5.4439	19.1990
1.6522	772.6	1.2943	5.3826	19.2029
1.4378	759.3	1.3170	5.1553	19.2179
1.4346	759.3	1.3170	5.1521	19.2147
1.3711	756.2	1.3224	5.0855	19.2058
1.3365	754.4	1.3256	5.0492	19.2037

Δ_{sH} 298 = 48.15 Kcal/mole.

95% confidence limit = 0.29 Kcal/mole.

TABLE XXXIX

LITHIUM FLUORIDE

Reference	Run	n	temp, °K	$\Delta_s H_{298}$ second law	kcal/mole third law
This work	3 4G xi	18	968-1046	65.14 ± 0.82	
	3 4G xii	13	965-1044	67.81 ± 0.88	
	3 4G xiii	14	966-1046	67.50 ± 1.10	
	3 4G xiv	20	969-1046	69.28 ± 0.75	
weighted mean value				67.49 ± 3.69	64.9
This work	3 Pt. vii	25	1001-1125	70.81 ± 0.44	
	3 Pt viii	23	1002-1126	70.27 ± 0.31	
	3 Pt. ix	20	1002-1123	70.33 ± 0.29	
weighted mean value				70.37 ± 0.73	64.8
Ruff, Schmidt & Mugdan		14	1671-1939	66.99 ± 0.69	63.7
v. Wartenburg and Schultz		5	1626-1820	67.18 ± 0.78	64.2

This work $\log_{10} p\ (mm) = 11.567 - \frac{14,697}{T}$

TABLE XL

SODIUM FLUORIDE

Reference	Run	n	temp. °K	$\Delta_s H_{298}$ second law	kcal/mole third law
This work	3 4G xxv	22	993-1082	66.09 ± 0.86	
	3 4G xxvii	18	1004-1082	65.50 ± 0.68	
	3 4G xxviii	27	1000-1083	67.05 ± 0.76	
weighted mean value				66.22 ± 1.95	67.2
This work	3 Pt. x	23	1023-1165	68.49 ± 0.47	
	3 Pt. xi	21	1028-1164	68.98 ± 0.46	
	3 Pt. xii	19	1028-1166	69.26 ± 0.49	
weighted mean value				68.91 ± 0.99	67.1
Niwa		5	1053-1112	64.15 ± 0.97	65.6
Miller and Kusch		4	1115-1189	68.88 ± 0.45	68.6
Sense et al		6	1220-1265	72.82 ± 0.96	66.2
Ruff Schmidt & Magdan		14	1699-1974	69.80 ± 0.94	65.7
v. Wartenburg & Schultz		5	1672-1835	71.96 ± 0.08	66.2
Sense et al.		9	1274-1348	68.85 ± 0.79	65.9

This work $\log_{10} p$ (mm) = 10.811 - 14350/T

TABLE XLI

POTASSIUM FLUORIDE

Reference	Run	n	temp.°K	$\Delta_s H_{298}$ second law	kcal/mole third law
This work	3 4G xv	19	877-944	58.16 ± 0.57	
	3 4G xvi	14	877-945	57.75 ± 0.48	
	3 4G xvii	21	877-992	58.15 ± 0.31	
weighted mean value				58.09 ± 0.45	57.6
This work	3 Pt xiii	20	902-1023	59.11 ± 0.22	
	3 Pt xiv	15	905-1022	58.74 ± 0.29	
	3 Pt xvi	18	902-1023	59.00 ± 0.30	
weighted mean value				58.97 ± 0.47	57.6
Niwa		6	913-973	56.03 ± 0.18	55.1
Ruff Schmidt & Mugdan		6	1551-1773	60.39 ± 2.61	56.5
v. Wartenburg & Schultz		5	1624-1776	56.24 ± 0.87	56.7

This work $\log_{10} p(mm) = 10.499 - \frac{12,275}{T}$

TABLE XLII

RUBIDIUM FLUORIDE

Reference	Run	n	temp.°K	$\Delta_s H_{298}$ second law	kcal/mole third law
This work	3 Pt xvi	18	853-959	55.62 ± 0.25	
	3 Pt xvii	16	854-960	55.31 ± 0.52	
	3 Pt xviii	15	854-959	55.81 ± 0.33	
weighted mean value				55.64 ± 0.65	54.83
Ruff Schmidt and Mugdan		4	1598-1673	52.1 ± 3.2	54.6
v. Wartenburg & Schultz		11	1436-1683	54.08 ± 0.58	54.55

This work $\log_{10} p(mm) = 10.527 - 11551/T$

TABLE XLIII

CAESIUM FLUORIDE

Reference	Run	n	temp, °K	$\Delta_s H_{298}$ second law	kcal/mole third law
This work	3 Pt iv	19	754-854	49.07 ± 0.18	
	3 Pt v	16	759-855	48.51 ± 0.26	
	3 Pt vi	22	753-856	48.15 ± 0.29	
Weighted mean value				48.73 ± 1.02	49.12
Ruff Schmidt and Mugdan		6	1355-1528	42.9 ± 1.3	50.4
v. Wartenburg and Schultz		7	1319-1524	45.7 ± 0.4	48.3

This work $\log_{10} p$ (mm) = 10.437-10208/T

TABLE XLIV

Substance	$\Delta_s H_{298}$ second law	(Platinum vessel) third law	kcal/mole Difference
LiF	70.4	64.8	5.6
NaF	68.9	67.1	1.8
KF	59.0	57.6	1.4
RbF	55.6	54.8	1.2
CsF	48.7	49.1	- 0.4
KCl	54.4	52.7	1.7

Discussion of results.

The agreement between this and previous work is reasonable as may be seen in Figures 22 and 23 where the results for sodium and potassium fluorides are plotted. Niwa's results both for sodium and potassium fluoride are high. He used a platinised quartz effusion cell which, he states, showed signs of having been attacked during the experiments. It seems likely therefore that the high vapour pressure was partly due to SiF_4 produced in reactions of the type.

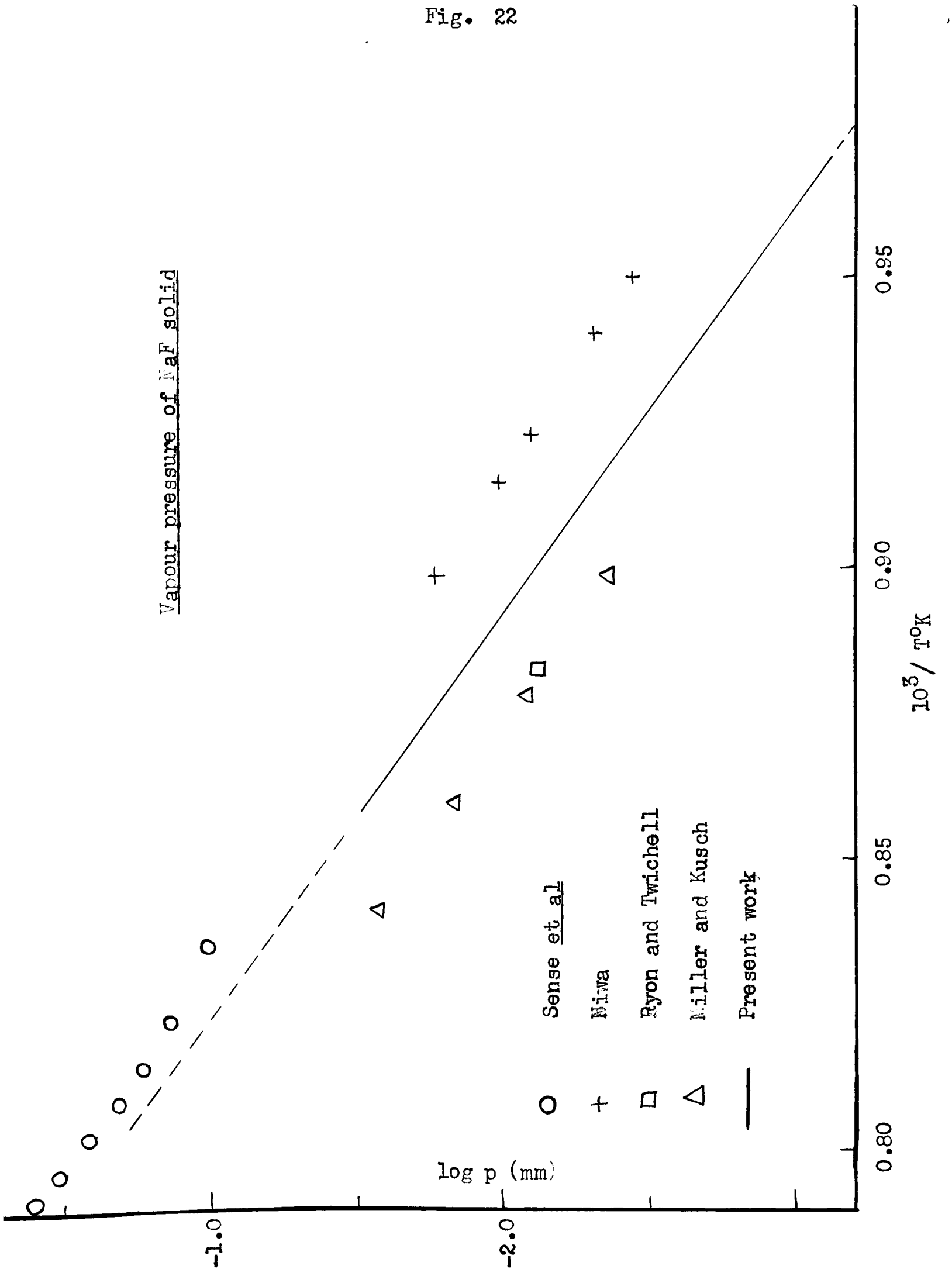
$$6NaF + 3SiO_2 = 2\ Na_2SiO_3 + Na_2SiF_6$$

$$Na_2SiF_6 = 2NaF + SiF_4.$$

As a further check on the agreement between the present work and that carried out on the liquid, the vapour pressure at the melting point was calculated from the equations given by Ruff Schmidt and Mugden (1922) and v.Wartenburg and Schultz (1921), and from those given in Tables XXXIX to XLIII. The results are given below.

Substance	log p(mm) at the melting point liquid data R S & M	v.W & S	present work
LiF	-1.648	-1.703	-1.521
NaF	-0.710	-0.579	-0.533
KF	-0.431	-0.207	-0.365
RbF	-0.328	-0.215	-0.496
CsF	+0.057	-0.171	-0.241

Fig. 22


Vapour pressure of NaF solid
log p (mm)
-1.0
-2.0
0.80
0.85
0.90
0.95
10^3 / T^oK
Sense et al
Niwa
Ryon and Twichell
Miller and Kusch
Present work

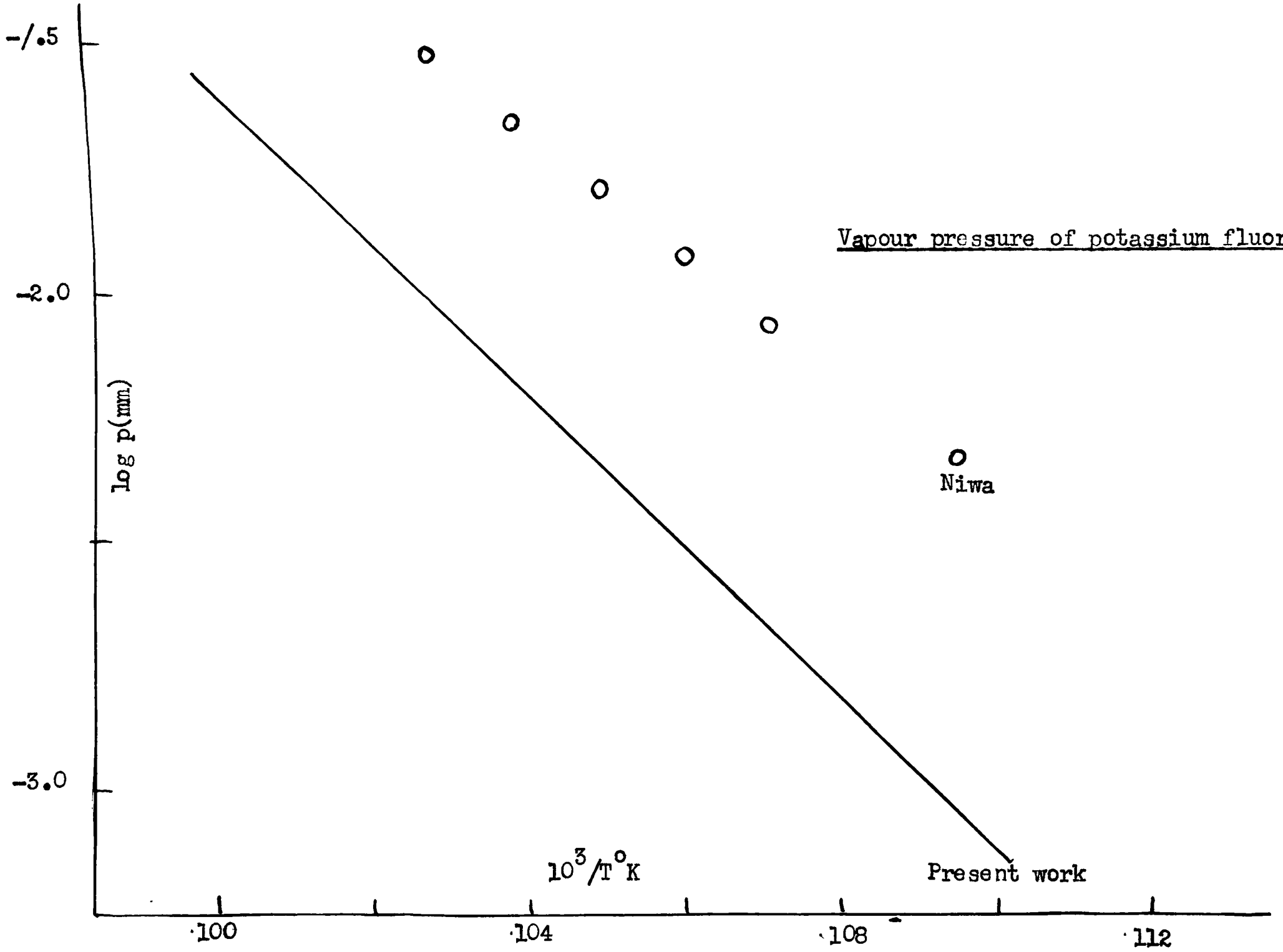

Vapour pressure of potassium fluoride
-/.5
-2.0
-3.0
log p(mm)
Niwa
Present work
$10^3/T^\circ K$
·100
·104
·108
·112

Fig. 23

Reference may here be made to Table XII where the results for potassium chloride are collected.

The most striking feature of Table XLIV is that the second law values are appreciably higher than the third law values, the difference being large for lithium fluoride and becoming less for the fluorides of the heavier metals. It is possible to reconcile the two values by assuming that the vapour contains appreciable concentrations of dimer and perhaps higher polymers, and this is discussed below.

A consideration of the errors in the measured heats of sublimation.

Systematic errors can arise from three causes:

1) Errors in the absolute calibration constant

2) Errors in the measurement of temperature

3) Errors arising from the use of inaccurate thermal data.

1) The principal error here is in the measurement of the area of the holes. It is estimated that the error is not greater than 0.5%. The error in measuring the thickness of the hole is more difficult to estimate, but in any case, the f factor is not very sensitive to changes in the ratio (thickness/diameter) and it is thought that little error was introduced here. Comparison with the work of other authors has shown that the calibration constant is fairly accurate. An error of 2% in the absolute pressure produces an error of only .04 k.calat 1000°K in the third law value of the heat of sublimation.

2) Errors in the measurement of temperature.

These could be more serious, since they affect the second law values of the heat of sublimation. Each calibration point could be determined within $\pm \frac{1}{2}^{o}C$. This means a maximum error between two calibration points of $1^{o}C$. The calibration points are roughly $250^{o}C$ apart, and each run stretches over about $125^{o}C$ so that the error between the ends of a run is about $\frac{1}{2}^{o}C$. The errors in interpolation should not be greater $\frac{1}{2}^{o}C$.

The total possible error between the ends of a run due to calibration errors is thus about $1^{o}C$ which is roughly equivalent to a change of $0.5_{k.cal}$/mole in the second law value of the heat of sublimation.

It is known that base metal thermocouples change their calibration with use. A check calibration run using potassium chloride was carried out at the end of the series of experiments and gave results identical with the calibration runs carried out at the beginning of the series, so it was considered that the thermocouples had not aged appreciably during the course of the work.

3) Errors arising from the use of inaccurate thermal data.

Errors in the heat capacity equations for the solid and gas tend to cancel in the third law treatment since the error appears in both the entropy and heat content terms.

In the table below are given the maximum possible errors

arising from inaccurate thermal data. The limits of error given by Kelley (1949) in his heat content equations for the solids were used where possible. The error in the entropy was calculated assuming the worst possible case where Cp from the equation is always either higher or lower than the true value over the entire temperature range from room temperature to the temperature of the high point.

For the gases in which the vibrational frequency was estimated, the entropy and heat content changes associated with a change in frequency of $\pm 50 cm^{-1}$ have been found.

	Error in second law value of $\Delta_s H_{298}$ Kcal/mole	Error in third law value of $\Delta_s H_{298}$ Kcal/mole
KCl	0.19	0.17
LiF	0.17	0.26
NaF	0.42	0.62
KF	0.37	0.56
RbF	0.27	--
CsF	0.17	--

The errors in the entropies of the crystal at room temperature estimated by the original authors has been included in the error in the third law values.

The gas molecules were assumed to carry out simple harmonic motion. The effect of anharmonicity and centrifugal stretching on the entropy of potassium chloride vapour at $1000^{o}K$ was found to increase the entropy by 0.13 e.u. The actual error in the third law value of the heat of sublimation will be smaller than 0.13 Kcal/mole at $1000^{o}K$ since the heat content of the true anharmonic gas is greater than that of the ideal S.H.M. gas (Mayer and Mayer (1946)).

The standard entropies of rubidium and caesium fluorides.

There is no experimental data for the standard entropies of crystalline rubidium or caesium fluorides. The values for this quantity calculated by the reverse of the usual third law treatment, assuming the heat of sublimation from the second law treatment, are shown below. They are compared with Latimer's (1951) estimated values: the agreement is fair.

	S^{o}_{298} calc.	S^{o}_{298} Latimer
RbF	16.5 e.u.	17.4 e.u.
CsF	19.6 e.u.	19.1 e.u.

PART XXI

ASSOCIATION IN THE VAPOURS OF THE ALKALI HALIDES

THE DISSOCIATION ENERGIES OF THE ALKALI FLUORIDES

Previous evidence for the existence of polymers in the vapours of the alkali halides.

Deitz (1956) carried out experiments on the vapour pressure of potassium chloride using an absolute manometer and a Knudsen effusion cell. The results obtained by the two methods agreed closely and he concluded that there was less than 10% of dimer in the gas; though as he says, the method is insensitive, and even if the vapour were entirely dimer, the two methods would give values of the vapour pressure differing by a factor of only $\sqrt{2}$.

Zimm and Mayer (1944) measured the vapour pressure of potassium chloride over a wide temperature range. They calculated the entropy of the gas at 800°K assuming it to be a mixture of monomer and dimer, and showed by a comparison between the experimental entropy and the calculated entropy that the degree of association must be small ($\not> 2\%$)

Recently more direct evidence for the presence of dimers has been found using mass spectrometer and molecular beam techniques. Friedmann (1955) investigated the mass spectrum of lithium iodide vapour effusing from a Knudsen effusion cell. He found large concentrations of Li_2I^+ and $Li_3I_2^+$ which he concluded could have been formed only from dimers or trimers. He concluded that the vapour contains approximately equal concentrations of monomer and dimer, but owing to the absence of data on their ionisation cross-sections was unable to measure their true concentrations. Hobson (1955) carried out similar experiments on the vapour of the chlorides of lithium, sodium and potassium. He found large intensities of ions of the type $Li_mCl_n^+$ and $Li_mCl_n^-$, where $(m + n) > 2$, in the vapour of lithium chloride. He proposed that these complex ions might be formed by a clustering process in which

atomic and molecular ions combine with neutral diatomic molecules, but was unable to explain all the features of the mass spectrum in this way and considered it likely that there were polymers in the vapour.

Ochs, Coté and Kusch (1953) in their molecular beam resonance studies on sodium fluoride, chloride, and iodide observed a peak in the sodium resonance graph which could not be explained by the theory for diatomic molecules. It was found that for a given temperature of the slit section of the oven producing the molecular beam, the intensity of the peak increased with the pressure in the oven as one would expect if it were due to a dimer. They estimated that dimers constituted 25-75% of the total beam. Later Kusch (1953) reconsidered the data on sodium fluoride and gave the fraction of the total beam which consists of dimers as 10%.

The most important evidence for the existence of polymers in the gas phase is due to Miller and Kusch (1956). These authors analysed the velocity distribution in molecular beams of ten alkali halides and found significant concentrations of dimer in all except the caesium salts and measurable concentrations of trimer for lithium chloride, lithium bromide and sodium fluoride. From a study of the composition of the vapours at a series of temperatures, it was possible to calculate the energy of dimerisation ($\Delta_2 E_T$) using the equation

$$\frac{d\,(\ln K_c)}{dT} = \frac{\Delta_2 E_T}{RT^2}$$

where K_c is the equilibrium constant expressed in terms of contrentation for the reaction

$$2\ MX \rightleftharpoons M_2X_2$$

A summary of the results obtained by these authors is given in the table below. The ratios p_1/P, p_2/P, and p_3/P (where p_1, p_2, p_3, P are the pressures of monomer, dimer, trimer and the pressure of all three, respectively) were calculated using the formulae

$$\frac{p_1}{P} = \frac{1-\delta-\eta}{1-\delta/2-2\eta/3}, \quad \frac{p_2}{P} = \frac{\delta/2}{1-\delta/2-2\eta/3}, \quad \frac{p_3}{P} = \frac{\eta/3}{1-\delta/2-2\eta/3}$$

where δ and η are the fractions of diatomic molecules which are associated to dimer and trimer respectively. The original paper gives the method of calculating δ and η . Δ_3E_T is the heat of dissociation of trimer to monomer and dimer

Table XLV

	Temperature at which total pressure is 10^{-2} mm	$\frac{p_1}{P}$	$\frac{p_2}{P}$	$\frac{p_3}{P}$	Δ_2E_T kcal	Δ_3E_T kcal
RbCl	866°K	0.919	0.081		48.1±0.6	
KCl	897	0.890	0.110		45.8±0.7	
KI	823	0.941	0.059		45.2±0.9	
NaF	1146	0.872	0.083	0.045	42.9±1.8	87.0±6.6
NaCl	920	0.737	0.264		44.7±0.9	
NaI	817	0.724	0.276		42.0±1.4	
LiCl	870	0.204	0.744	0.053	38.2±0.3	34.2±1.9
LiBr	803	0.210	0.728	0.062	42.3±1.1	36.3±0.5

The most notable feature is the high degree of dimerisation in the lithium halide vapours decreasing for the halides of the heavier elements. For the lithium halides, $\Delta_2 E_T$ tends to increase as the atomic weight of the halogen decreases. Friedman's data were used to calculate $\Delta_2 E_T$ for lithium iodide and the result was in agreement with this trend. ($\Delta_2 E_T = 43.1 \pm 1.2$ kcal at $920^{\circ}K$). It will be shown later that the results of the present work on lithium fluoride also agree with this trend.

No spectroscopic evidence of dimerisation has been found. Rice & Klemperer (1957)[1] calculated that it should be possible to detect the presence of dimers from the infra-red absorbtion spectrum but found no evidence of dimerisation

Honig, Mandel, Stitch and Townes (1954) state that the internuclear distances of the alkali halides measured by electron diffraction have been consistently higher than those obtained from micro-wave spectra. Since we should expect the internuclear distance in a dimer to be higher than that in the corresponding monomer, they consider that this is evidence in favour of the existence of dimers in the vapour.

<u>The effect of dimerisation on the present results.</u>

Consider the sublimation to a mixture of monomer and dimer of one mole of a crystalline alkali halide MX(c). Let the fraction of monomer which is associated to dimer be δ.

Using the third law treatment

$$\Delta_s H_m = T \Delta S = T(S_{(g)m} - S_{(c)}) \qquad (1)$$

where $\Delta_s H_m$ is the heat of sublimation of one mole of crystal to a mixture of monomer and dimer, $S_{(g)m}$ is the entropy of the mixture of gases and $S_{(c)}$ is the entropy of the crystal.

$$S_{(g)m} = (1 - \delta)(S_1^\circ - R\ln p_1) + \frac{\delta}{2}(S_2^\circ - R\ln p_2) \qquad (2)$$

Suffixes 1, and 2 refer to monomer and dimer respectively.

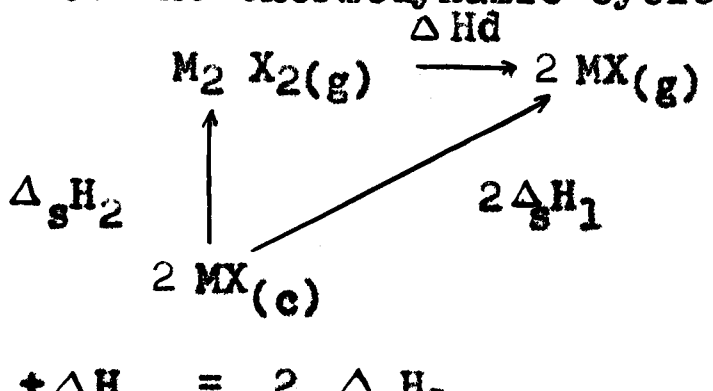
$$\frac{\Delta_s H_m}{RT} = \frac{(1 - \delta)(S_1^\circ - R\ln p_1) + \frac{\delta}{2}(S_2^\circ - R\ln p_2) - S_{(c)}}{R} \qquad (3)$$

all quantities are measured at the temperature T.

The experimental second law value of the heat of sublimation is produced by plotting log $(p_1 + p_2)$ against $1/T$ and as can be seen from equation (3) above cannot be identified with the heat of sublimation to a mixture of monomer and dimer. Indeed, since it is improbable that δ will remain constant with temperature, it is unlikely that the line will be straight. From the results of Miller and Kusch, the heat of sublimation of the dimer is usually greater than that of the monomer so we should expect the curve to become steeper at higher temperatures as the heat of sublimation to dimer makes a larger contribution to the observed slope. At the

same time, if dimer forms a significant portion of the total vapour pressure an erroneously large pressure will have been used in evaluating the third law value of the heat of sublimation assuming that the vapour consists wholly of monomer, resulting in a heat of sublimation by the third law treatment that is too small. It appears therefore, that lack of agreement between the experimental second and third law values of the heat of sublimation gives a qualitative indication of the presence of polymerisation in the vapour.

From the thermodynamic cycle



$$\Delta_s H_2 + \Delta H_d = 2\ \Delta_s H_1$$

$$\Delta H_d = \Delta E_d + RT \qquad (4)$$

where ΔE_d is the energy of dimerisation.

Also, for the reaction

$$M_2 X_{2(g)} \rightleftharpoons 2\ MX_{(g)}$$

$$\Delta G^\circ = \Delta H_d^\circ - T\ (2S_1^\circ - S_2^\circ) \qquad (5)$$

or $$- RT \ln K_p = - RT \ln \frac{p_1^2}{p_2} = - T(2\ S_1^\circ - S_2^\circ) + \Delta H_d \qquad (6)$$

If therefore we have values of ΔH_d, the standard entropies of monomer and dimer, and the total pressure of monomer and

dimer we have sufficient information to calculate the pressures of monomer and dimer. By inserting the value of p_1 into the third law treatment for the heat of sublimation to monomer in place of the total pressure of monomer and dimer formerly used, the correct heat of sublimation is obtained.

O'Konski and Higuchi (1955) have calculated the energy of dissociation to gaseous ions of the dimer Na_2 Cl_2 by extending Rittner's (1951) treatment of the diatomic molecule. They found that the structure was a rhombus of apex angle 105°; the internuclear distance having increased from 2.3606Å in the monomer to 2.59Å. It was hoped to calculate the energy of dimerisation of lithium fluoride using a similar model. The rhombic structure of apex angle 105° was used.

A rough calculation of the heat of dissociation to ions of the dimer was first carried out, excluding the effects of polarizability in order to find approximately the internuclear distance. The total energy, including the terms due to polarizability was then found for a range of internuclear distances using the values given by Rittner (1951) for the polarizabilities of the ions, and the constants A and ρ in the Born repulsion term $Ae^{-r/\rho}$. The vander Waals attractive term was ignored as being small.

$A = 436$ ev.
$\rho = 0.311$
$\alpha_1 = .029 \times 10^{-24} cm^3$
$\alpha_2 = 1.05 \times 10^{-24} cm^3$

where α_1 is the polarizability of the lithium ion and α_2 is the polarizability of the fluoride ion.

The minimum energy was found to be 16.99 e.v. at an internuclear distance of 1.9Å . Rittner gives the energy of dissociation to ions of the diatomic molecule as 7.73 e.v, so using this value, the energy of the process

$$Li_2 F_2 \rightleftharpoons 2\ LiF$$

is $2 \times 7.73 - 16.99 = -1.53$ev. = 34.5 Kcal at $0^{\circ}K$. If the dissociation energy for the diatomic molecule given later in this thesis is used the value of 1.8 e.v. or 41.4 Kcal is obtained for the energy of dimerisation at $0^{\circ}K$. It was obvious therefore, by comparison with the results of Miller and Kusch that this treatment does not give a useful value of the energy of dimerisation, therefore the following treatment was used.

Equation (6) gives the pressures of monomer and dimer in terms of the total pressure and the heat of dimerisation. It is supposed that the standard entropies of monomer and dimer can be calculated. If a value of ΔH_d is chosen, the pressures p_1 and p_2 are immediately defined, and p_1 can be used in the third law calculation of the heat of sublimation of monomer. Furthermore, if the pressures p_1 and p_2 are

calculated at two temperatures, the values can be used in the Clausius-Clapeyron equation to find the heats of sublimation to monomer and to dimer (second law values). By varying ΔH_d, the heat of dimerisation, until agreement is obtained between the values of the heat of sublimation to monomer from the second and third law treatments, estimates of the degree of dimerisation, the heat of dimerisation and the heats of sublimation to monomer and dimer are obtained.

The change in ΔE, the energy of dimerisation, from $0^{o}K$ to $1050^{o}K$ for lithium fluoride was calculated to be only 0.75 k cal/mole, so ΔE was assumed constant over the range of the experiment.

The standard entropy of the monomer at 1mm pressure was calculated using the following equation

$$(S_1^o)_T = 4.57566 \left[\frac{3}{2} \log M + \frac{7}{2} \log T + \log I + 41.2042\right] + S(\text{Einst})$$

where M = molecular weight in atomic weight units

I = moment of inertia in c.g.s units

S(Einst) = vibrational entropy.

For the dimer a similar equation was used (Kelley (1949))

$$(S_2^o)_T = 4.57566 \left[\frac{3}{2} \log M + 4 \log T + \frac{1}{2} \log I_1 I_2 I_3 - \log\sigma\right] + S(\text{Einst}) + 278.554$$

where I_1, I_2, I_3 are the moments of inertia about the three

principal axes of the molecule. σ , the symmetry number has the value 4 in this case. In calculating the moment of inertia, O'Konski and Higuchi's(1955) planar rhombic structure of apex angle 105^{o} was used with internuclear distances 10% greater than in the monomer for all cases except lithium fluoride which has already been discussed.

The vibrational entropy per vibrational degree of freedom was found using the expression

$$S_{vib} = R \left[\frac{x}{e^{x} - 1} - \ln (1 - e^{-x}) \right]$$

where $= \dfrac{hc\omega_e}{RT}$

where h = Planck's constant
c = velocity of light
ω_e = vibrational frequency in cm^{-1}
k = Boltzmann's constant.

Zimm and Mayer (1944) proposed that of the six vibrational modes in the dimer , five are stretching modes and have the same frequency, and the sixth is a bending mode with a frequency of one tenth that of the stretching modes. In the present work the vibrational frequency was found using the expression of Birge and Mecke for finding the internuclear distance (r_e) of a molecule in an excited state when the internuclear distance in a lower state is already known

$$\omega_{e\,1} \cdot r_{e\,1}^{2} = \omega_{e\,2} \cdot r_{e\,2}^{2}$$

In the expression of Birge and Mecke the suffixes 1 and 2 refer to the two states of the molecule. In this case they refer to the monomer and dimer respectively. For lithium fluoride r_{e2} was determined by the theoretical calculation using the method of O'Konski and Higuchi (1955), described above. For the other molecules considered, the internuclear distance in the dimer was assumed to be 10% greater than that in the monomer. This equation is obviously not strictly applicable to the present case since it applies to two states within the same molecule, and here it is applied to the same bond in two different molecules. However, it is probably a reasonable approximation.

The standard entropies of monomer and dimer were calculated at the extreme temperatures used in the third law treatment of the observations, a plausible value of ΔE, the energy of dimerisation was chosen by reference to Miller and Kusch (1956) and this was then varied until agreement between the second and third law values of the heat of sublimation of monomer was obtained using the method described above.

The degree of dimerisation in the vapours of lithium fluoride, sodium fluoride, potassium fluoride and potassium chloride was studied. No such study was possible for rubidium and caesium fluorides since the entropy of the crystalline substances at 298°K had to be estimated. Miller

and Kusch found a small degree of dimerisation in the vapours of rubidium salts and none in those of caesium salts.

The results of the calculations are shown in Table XLVI The experimental heats of sublimation are those calculated directly from experimental results ignoring the presence of dimer . The corrected results are those calculated including the effect of dimerisation.

TABLE XLVI

Substance	T	Experimental $\Delta_s H_{298}$ 2nd law	Experimental $\Delta_s H_{298}$ 3rd law	Corrected $\Delta_s H_{298}$ 2nd law	Corrected $\Delta_s H_{298}$ 3rd law	ΔE_T Kcal/mole	K_p mm	P mm	P_1 mm	P_2 mm	$\frac{P_2}{P}$
LiF	1000	70.4	64.8	66.7	66.3	53	5.22×10^{-4}	7.42×10^{-4}	4.14×10^{-4}	3.28×10^{-4}	.42
	1120					53	9.48×10^{-3}	2.79×10^{-2}	1.22×10^{-2}	1.57×10^{-2}	.56
NaF	1030	68.9	67.1	67.9	67.3	52	1.13×10^{-2}	7.55×10^{-4}	7.10×10^{-4}	$.45 \times 10^{-4}$	.06
	1165					52	0.196×10^{-2}	3.11×10^{-2}	2.73×10^{-2}	$.38 \times 10^{-2}$	.12
KF	900	59.0	57.6	58.1	57.8	45	1.03×10^{-2}	7.24×10^{-4}	6.79×10^{-4}	$.45 \times 10^{-4}$	.06
	1020					45	0.195×10^{-2}	2.78×10^{-2}	2.47×10^{-2}	$.31 \times 10^{-2}$	.11
KCl	830	53.85	52.7	53.9	53.3	49	1.486×10^{-3}	6.47×10^{-4}	4.88×10^{-4}	1.59×10^{-4}	.25
	940					49	4.436×10^{-2}	2.56×10^{-2}	1.82×10^{-2}	0.74×10^{-2}	.29

Discussion of the method.

The method is obviously not very accurate. In the first place it is difficult to estimate the vibrational entropy in the dimer , which is a large fraction of the total entropy of the dimer . Miller and Kusch (1956) used the method described by Zimm and Mayer to calculate the entropy of potassium chloride dimer at 933°K and obtained the value 115 ± 6 e.u. at a standard pressure of 1mm. Their experimental value was 112.7 ± 1.1 e.u. This agreement may be fortuitous, but it seems to show that the assumptions regarding the vibrational entropy are fairly good.

The sensitivity of the method in determining the partial pressures of monomer and dimer appears to depend upon two factors.

a) For potassium chloride, it was found that a postulated change in the fraction of the pressure due to monomer from 0.91 to 0.71 produced a change of only 0.35 Kcal/mole in the heat of sublimation of monomer by the second law. The reason for this appears to be that for this substance the heats of sublimation of monomer and of dimer are very similar. If they were identical the ratio p_1/p_2 would remain constant with temperature, and no matter what value of p_1 / p_2 were proposed, the heat of sublimation of monomer obtained using the Clausius-Clapeyron equation would remain the same. In fact it is not as simple as this, since the ratio p_1/p_2

is changed by assuming a different value of ΔH_d which alters the relative values of the heats of sublimation to monomer and to dimer.

The method is insensitive in the case of potassium chloride since the second law value changes only slightly with change in the p_1/p_2 ratio and the fitting of the second and third law values is done mainly by change in the third law value which is insensitive to changes in the value of p_1 This makes the method prone to errors in the measured pressures.

In the case of <u>lithium fluoride</u> it was found that the heat of sublimation of monomer was considerably smaller than that of the dimer. If an increase in the degree of dierisation was assumed, the calculated second law value of the heat of sublimation to monomer decreased, while the third law value increased. It was possible in this case to get a much more accurate estimate of the degree of dimerisation, since for a given change in the p_1/p_2 ratio, the second and third law values of the heat of sublimation move in opposite directions, and errors in the measured pressures are less important.

The method is, it seems, more sensitive when the difference between the heats of sublimation of monomer and dimer is large.

b) The accuracy of the method depends on the magnitudes of

p_1 and p_2. If it is assumed, say, that the concentration of monomer is very small, then the pressures of monomer calculated at the two experimental temperatures will be very small and may be of the order of the experimental error. The second law value of the heat of sublimation calculated from these two pressures using the Clausius Clapeyron equation will be inaccurate. Maximum information on the heats of sublimation of monomer and dimer would seem to be available when the pressures of monomer and dimer are equal. If information concerning the monomer only is required then a small degree of dimerisation is desirable.

<u>The dissociation energy of the alkali fluorides.</u>

From a thermo chemical cycle the following expression is obtained for the heat of dissociation to atoms of the alkali fluorides.

$$D(M+F) = \tfrac{1}{2}D(F_2) + Q_f(MF) + L(M) - L(MF)$$

and $D(M^+ + F^-) = D(M+F) + E(F) - I$

where $D(M+F)$ is the heat of dissociation to atoms of the alkali fluoride.

$D(F_2)$ is the heat of dissociation to atoms of fluorine gas.

$Q_f(MF)$ is the standard heat of formation of the alkali fluoride.

$L(M)$ is the heat of sublimation to atoms of the metal.

$L(MF)$ is the heat of sublimation of the alkali fluoride.

I is the ionisation potential of the alkali metal.

E(F) is the electron affinity of fluorine.

$D(M^+ + F^-)$ is the heat of dissociation, to ions.

	$\frac{1}{2}D(F_2)$	$Q_f(MF)$	L(M)	L(MF)	I	E(F)	$D(M^+F)$	$D(M^+ + F^-)$
Li F	18.7	146.3	36.44	66.3	125.79	82.8	132.1	175.1
NaF	18.7	136.0	25.98	67.4	119.98	82.8	113.3	150.5
KF	18.7	134.46	21.51	57.8	101.55	82.8	116.9	135.6
RbF	18.7	131.28	20.51	55.6	97.79	82.8	115.1	130.1
CsF	18.7	126.9	18.83	48.7	91.26	82.8	115.3	123.8

All quantities are measured in kcal/mole at 298.16 ^{o}K

Notes:- The dissociation energy of fluorine was determined by Doescher (1952) and his value was corrected by Barrow and Caunt (1953) to 298 ^{o}K. Values of the heat of formation of the alkali fluorides, and the heat of sublimation of the alkali metals are taken from the National Bureau of Standards Circular 500 (1952).

The ionisation potentials of all the metals are taken from Moore (1949); The electron affinity of fluorine, was found from a Born-Haber cycle on each of the alkali fluorides using the lattice energies (A) given by Evans, Warhurst and Whittle (1950) who have corrected the values of Huggins (1937) to room temperature.

$E(F) = Q(MF) + L(M) + I + \frac{1}{2}D(F_2) - U$

	LiF	NaF	KF	RbF	CsF
Q(MF)	146.3	136.0	134.46	131.28	126.9
L(M)	37.07	25.95	21.52	20.50	18.83
I	125.79	119.98	101.55	97.79	91.26
$\frac{1}{2}D(F_2)$	18.7	18.7	18.7	18.7	18.7
U	245.1	216.4	193.2	183.4	175.9
E	82.13	84.23	83.03	84.88	79.79

mean value of E = 82.8 kcal/mole.

Comparison between thermo chemical and spectroscopic values of the dissociation energy.

The ultra violet absorption spectra of potassium rubidium and caesium fluorides were studied by Barrow and Caunt (1953) whose values for the dissociation energy are compared below with the thermo-chemical values calculated in the previous section.

	Spectroscopic	Thermo chemical
KF	122.6 kcal/mole	116.9 kcal/mole
RbF	125.7 "	115.1 "
CsF	129.9 "	115.3 "

In each case, the spectroscopic value is higher than the thermo-chemical.

The ultra violet spectra are formed by transitions between the stable ionic ground states and weakly bound upper states which dissociate to neutral atoms. These upper states are either purely repulsive or have very shallow minima. Barrow and Caunt had to assume that at the

highest vibrational quantum numbers observed the upper state curve was horizontal. They then plotted (G_v'' + v_{obs}) against the vibrational quantum number v, where G_v'' is given by

$$G_v'' = w_e (v + \tfrac{1}{2}) - w_e x_e (v'' + \tfrac{1}{2})^2 + y_e w_e (v'' + \tfrac{1}{2})^3$$

choosing values of w_e , the vibration frequency and $w_e x_e$ until the curve produced had the shape expected of the upper state potential energy curve. It seems in fact, that the upper states are more repulsive than they supposed. This would give values of the dissociation energy more in line with the thermo-chemical values and would also require smaller values of the vibration frequency. Barrow and Caunt's values of this quantity are higher than those obtained by Klemperer, which is a further indication that the energies of dissociation are lower than the values they give.

<u>The binding energy of the alkali halide molecules from the classical electro staticmodel.</u>

The theory of ionic lattices developed by Born and Mayer proposes that the forces between ions can be divided roughly into two parts:

a) attractive, consisting of purely coulombic terms and terms due to polarization etc.

b) a short range repulsive term.

Rittner (1951) applied the principles of the Born lattice theory to the alkali halide gas molecule and was able

to account satisfactorily for several of the important properties of the molecule. Two types of repulsive term have been used in the classical theoretical treatments of ionic molecules:

a) the Born relationship $B(r) = b/r^n$ where b and n are constants.

b) the Born-Mayer relationship $B(r) = Ae^{-r/\rho}$ where A is a constant for each substance.

Rittner used the exponential expression. Varshni has recently used the electrostatic model to calculate values of the rotational constant α_e and the vibrational constant $\omega_e x_e$ for the alkali halides and used both forms of repulsive term. He concluded that the exponential function gave better results.

Rittner's expression for the binding energy U of a gaseous diatomic halogen molecule is given below (equation 1).

$$U = -\frac{e^2}{r} - \frac{e^2(\alpha_1+\alpha_2)}{2r^4} - \frac{2e^2\alpha_1\alpha_2}{r^7} - \frac{c}{r^6} - \frac{h\nu_0}{2} + \frac{h\nu_0}{\exp(h\nu_0/kT)-1} - \frac{kT}{2} + Ae^{-r/\rho} \quad (1)$$

where e is the charge on each ion
α_1 , α_2 are the polarizabilities of metal and ions respectively
c is the van der Waals constant
A and ρ are constants
Vo is the vibration frequency
r is the internuclear distance.

The terms not already referred to are a van der Waals attractive term, and terms representing the difference in translational rotational and vibrational energy between the molecule and the free ions from which it is composed.

The binding energy of the alkali fluorides was calculated using up to date values of the quantities in the above equation.

The values of the polarizabilities used were those given by Tessman Kuhn and Shockley (1953).

London (1930) and Born and Mayer (1932) have stated that the van der Waals constant c may be calculated from the equation

$$c = \frac{3\,\epsilon_1.\epsilon_2.\alpha_1.\alpha_2.}{2(\epsilon_1+\epsilon_2)} \qquad (2)$$

where ϵ_1 is the second ionisation potential of the alkali metal

ϵ_2 is the electron affinity of the halogen

Born and Mayer (1932) found that the London dispersion forces calculated using the value of c so obtained were about 50% too low. Mayer (1933) reconsidered the method of calculation and gave new values for c. In the present work the precept of Rittner and Varshni was followed and C was calculated using equation (2). For caesium fluoride, the binding energy was calculated using Mayer's value of c and also using the calculated value which was about one third of Mayer's value. The difference between the resulting values of the binding energy was 0.5 kcal/mole.

The value of ρ used was that given by Rittner ($\rho = 0.311$).

The constant A was found for each molecule by differentiating equation (1) and equating to zero for minimum energy.

The binding energy was corrected to 298°K as follows.

$$U^{o}_{298} - U^{o}_{o} = \sum (H^{o}_{298} - H^{o}_{o})$$

The summation term denotes the difference, at 298 and at 0°K between the heat content of the molecule and of the separate ions.

Now $H = E + PV = E + RT$.

For a molecule of gas, $H = \frac{5}{2} RT + E_i$ where E_i is the internal energy.

For both ions and for the molecule, the electronic states are singlets so that the electronic contribution will be zero.

For each ion $H = \frac{3}{2} RT$.

For the molecule $H = \frac{7}{2} RT + \frac{h c \omega_e}{e^{-hc\omega/k.298} - 1}$

where c = velocity of light and k is the Boltzman constant.

$$\sum (H^{o}_{298} - H^{o}_{o}) = \frac{3}{2} (R \times 298.16) - \frac{hc\omega_e}{e^{-hc\omega/k298} - 1}$$

The results of the calculations and the quantities used are given in Table XLVII below.

Table XLVII

	α_1 $cm^3 \times 10^{24}$	α_2 $cm^3 \times 10^{24}$	ϵ_1 erg $\times 10^{-12}$	ϵ_2 erg $\times 10^{-12}$	r_e Å	c erg $\times 10^{60}$	A erg $\times 10^{11}$	U^o_{298} calc	U^o_{298} thermo-chemical	Δ
								kcal/mole		
LiF	.03	0.64	121.141	5.751	1.527	0.25	58.631	177.8	175.1	2.7
NaF	0.41		75.759		1.840	2.10	114.46	155.3	150.5	4.8
KF	1.33		50.959		2.129	6.60	233.58	140.6	135.6	5.0
RbF	1.98		43.751		2.246	9.66	320.18	136.0	130.1	5.9
CsF	3.34		37.487		2.3453	15.99	485.10	132.1	123.8	8.3

In the first instance the binding energy was calculated omitting the van der Waals attractive energy, the zero point energy and the term in $\alpha_1\alpha_2$ in the calculation of both A and the binding energy. The greatest difference between the energy so calculated and that calculated including these terms was 1.2 kcal/mole for caesium fluoride.

There is a systematic increase in the difference between the experimental and calculated dissociation energies from lithium fluoride to caesium fluoride. This seems to show that there is some defect in the model. It would appear that possibly the coulombic forces have been over estimated and that for the heavier metallic ions screening of the nucleus has become more pronounced.

APPENDIX

THE MULLIKEN BAND SYSTEM OF C_2

Introduction.

The C_2 molecule has considerable astrophysical importance: its spectrum has been observed in the sun and other stars, and in the tails of comets. It is therefore of interest to determine its constants as accurately as possible. Two series of spectra are observed arising from singlet-singlet and triplet-triplet transitions, and so far no inter-combination between these two series has been observed. There is therefore some doubt as to the relative energies of the singlet and triplet levels.

The Mulliken bands occur at wave lengths in the region of 2300 A, and arise from transitions between the ground state of the singlet series $^1\Sigma_g^+$ and the $^1\Sigma_u^+$ level. They were first reported by Mulliken (1930). Subsequently they were measured by Hori (1934) and the first complete analysis was carried out by Landsverk (1939).

Plates of better resolution than those used by earlier workers became available, and it was hoped that besides extending the analysis to higher J values and hence obtaining better values of the rotational constants, it might be possible to detect perturbations of the singlet levels by the triplet levels. These might yield evidence for the relative energies of the two systems.

Phillips has analysed the band system due to transitions between the ground state $^1\Sigma_g^+$ and the $^1\Pi_u$

Experimental.

The plates used were taken at the University of Stellenbosch South Africa by Professor P.B. Zeeman using the fourth order of a 21ft. concave grating. The spectrum was excited by passing a discharge through a mixture of benzene vapour and argon. The comparison spectrum was an iron arc in the second order.

The bands.

The system consists of a series of headless bands. Since it is a $^1\Sigma - {}^1\Sigma$ transition, no Q branch is produced. C_2 is a homonuclear molecule with zero nuclear spin, and therefore alternate lines are missing, only those of even J being observed.

Method.

The methods used to analyse the rotational structure of bands have been dealt with very adequately by Herzberg (1950). Definitions of the symbols, and proof of the equations used here will be found in his work.

The frequencies of the R and P branches are given by the following equations

R branch: $\nu = \nu_0 + F_v'(J+1) - F_v''(J) = R(J)$

P branch: $\nu = \nu_0 + F_v'(J-1) - F_v''(J) = P(J)$

here J is the rotational quantum number in the lower state.

Firstly, the combination differences for the upper and lower states were found using the relations

$$R(J-1) - P(J+1) = \Delta_2 F''(J)$$

$$R(J) - P(J) = \Delta_2 F'(J).$$

Now $\Delta_2 F(J) = (4B_v - 6D_v)(J+\frac{1}{2}) - 8D_v(J+\frac{1}{2})^3$

Therefore a plot of $\frac{\Delta_2 F(J)}{(J+\frac{1}{2})}$ against $(J+\frac{1}{2})^2$ has a slope of $8D_v$ and an intercept of $(4B_v - 6D_v)$. Phillips' bands have the same ground state as the Mulliken bands and the combination differences from his work were combined with the present results to give the rotational constants B_v and D_v for the $^1\Sigma_g^+$ state. Values of B and D for the upper state were found from values of $\Delta_2 F(J)$. These first values of the constants were used to calculate the position of lines in the P and R branches which had not then been identified.

The band origin was found, and the differences $(B_v' - B_v'')$ and $(D_v' - D_v'')$ were found more accurately by plotting $R(J) + P(J)$ against $J(J+1)$. According to the following relation

$$R(J)+P(J) = 2\nu_0 + (2B_v' - 4D_v') + 2(B_v' - B_v'' - 6D_v')\,J(J+1) - 2(D_v' - D_v'')\,J^2(J+1)^2$$

The result was a curve whose departure from linearity at high J numbers gives the value of $(D_v' - D_v'')$.

The slope of the straight line produced by plotting $R(J)+P(J)+2(D_v' - D_v'')J^2(J+1)^2$ against $J(J+1)$ gave $(B_v' - B_v'' - 6D_v')$. These differences $(B_v' - B_v'')$ and $(D_v' - D_v'')$ were combined with the accurate values of B_v'' and D_v'' for the lower state from the combination differences to give B_v' and D_v' .

The values of B_v' and D_v' were further refined by calculating the positions of the R and P branches and adjusting the values of the constants to obtain the best fit with the experimental measurements.

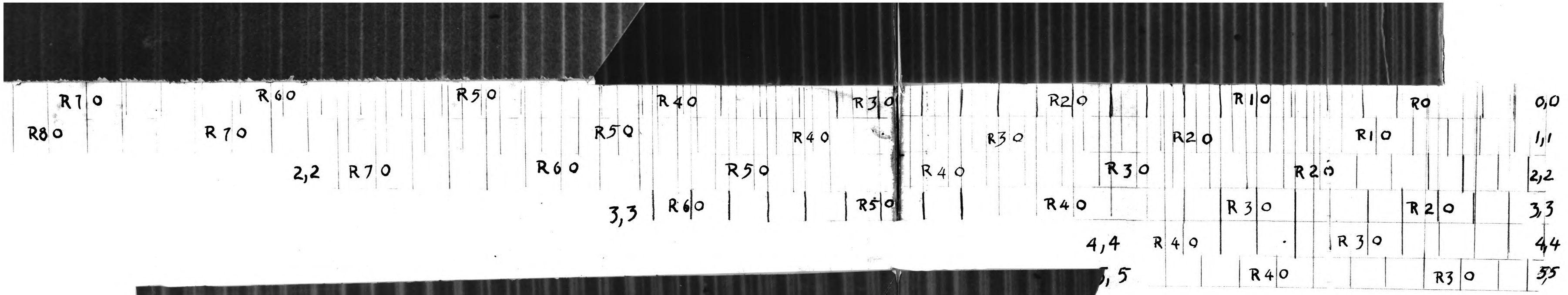
The positions of the 4-4 and 5-5 bands were found by extrapolating the graph of the frequency of the R line at any particular J value against the vibrational quantum number.

Results.

No evidence for perturbations was found. The analysis has been extended to the 4-4 and 5-5 bands.

The results are given in Tables 1 to 6. In Table 7 the rotational constants are given. All frequencies are in cm^{-1}.

In Tables 1 to 6 are listed the observed frequencies, with the differences from the calculated frequencies, of the R and P branches for each band. An asterisk denotes a blended line and a letter d following the number represents a diffuse line. $\Delta_2 F(J)$, for each band is also listed, including, where relevant, Phillips' values. Wherever possible, second differences derived from blended lines were not used to calculate B_v'' and D_v'' .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R60
R50
R40
R30
R20
R10
R0
0,0
R80
R70
R50
R40
R30
R20
R10
1,1
2,2 R70
R60
R50
R40
R30
R20
2,2
3,3 R60
R50
R40
R30
R20
3,3
4,4 R40
R30
4,4
R40
R30
5,5

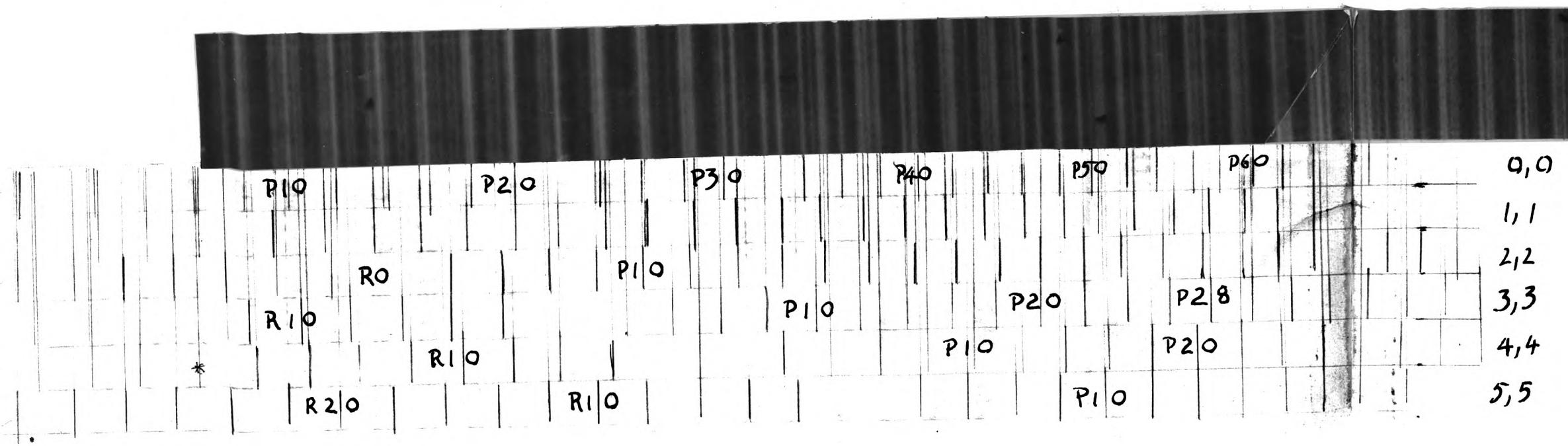
P10
P20
P30
P40
P50
P60
0,0
1,1
2,2
3,3
4,4
5,5
R0
P10
R10
P10
P20
P28
R10
P10
P20
R20
R10
P10

TABLE 1

0 - 0 Band

J	R(J)	o - c	P(J)	o - c
0	43230.61	-.01		
2	38.01	+.02	19.60x	-.15
4	45.47	+.03	12.57	-.06
6	52.94	-.06	05.61x	+.02
8	60.76	+.11	43198.65	-.03
10	68.38x	-.24	91.79	-.06
12	76.10x	-.09	85.16	+.04
14	84.13	+.03	78.51	+.01
16	92.07	+.00	71.91	-.07
18	43300.07	-.07	65.54	-.02
20	08.33	+.07	59.20x	-.04
22	16.54	+.06	53.06x	+.03
24	24.81	+.04	47.02	+.05
26	33.20	+.08	40.90	-.03
28	41.54	+.00	35.01	-.01
30	50.03	+.01	29.29	+.06
32	58.59	+.02	23.43	-.10
34	67.25	+.09	18.03	+.08
36	75.86	+.05	12.45	-.01
38	84.61	+.10	07.04	-.03
40	93.21	-.01	01.74	-.04
42	43402.10	+.04	43096.58	-.02

$\Delta_2 F''(J)$

J	Phillips 2,0	Phillips 3,0	$^1\Sigma - {}^1\Sigma$ 0,0	mean
1				
3	25.34		25.44	25.39
5	39.83	39.87		39.85
7	54.28	54.35	54.29	54.31
9	68.79	68.82	68.97	68.86
11	83.21	83.22		83.22
13	97.66	97.65		97.65
15	112.11		112.22	112.17
17	126.49		126.53	126.51
19	140.86	140.87		140.87
21	155.26	155.23		155.24
23	169.57	169.47	169.52	169.52
25	183.82	183.78		183.80
27	198.10	198.06	198.19	198.12
29	212.30	212.24	212.25	212.26
31	226.48		226.60	226.54
33		240.56	240.56	240.56
35		254.62	254.80	254.71
37		268.70	268.82	268.76
39			282.87	282.87
41			296.63	296.63
43			310.59	310.59

TABLE 1 (continued)

J	R(J)	o - c	P(J)	o - c	J	$\Delta_2 J''$ (J) Phillips 2,0	3,0	$^1\Sigma - ^1\Sigma$ 0,0	mean
44	10.95	+.08	91.51	+.01	45				
46	19.72	+.02	86.63x	+.13	47			338.08	338.08
48	28.61	+.04	81.64	+.04	49			351.82	351.82
50	37.46	-.01	76.79	+.01	51			365.33	365.33
52	46.23	-.16	72.13	+.06	53			378.80	378.80
54	55.22	-.10	67.43	-.01	55				
56	64.05	-.21	62.60	-.31	57			405.72	405.72
58	73.16	-.05	58.33	-.11	59			419.16	419.16
60	81.78	-.38	54.00	-.07	61				
62	91.03	-.07	49.73x	-.05	63				
64	43500.16	+.14	45.33x	-.24	65				
66	08.97	+.04	41.08d	-.36	67				
68	17.79	-.02	37.47	+.1<	69				
70	26.72x	+.07			71				
72	35.50	+.01			73				
74	44.25	-.02			75				
76	52.95	-.05			77				
78	61.50	-.17			79				
80	70.26x	-.04			81				
82	(78.72)				83				
84	(86.73)				85				
86	(95.48)								

TABLE 2

1 - 1 Band

J	R(J)	o - c	P(J)	o - c
0				
2	43212.08	+.01	43194.07	+.05
4	19.45	+.02	86.97	+.02
6	26.92	+.04	80.05	+.08
8	34.41	-.02	73.13	+.02
10	41.91	-.14	66.32	+.01
12	49.74	+.00	59.40*	-.21
14	57.49	-.02	53.06	+.05
16	65.36	+.00	46.54	+.04
18	73.27	-.01	40.20	+.10
20	81.16	-.11	33.80	+.02
22	89.29	-.03	27.76*	+.10
24	97.38	-.05	21.35*	-.09
26	43305.61	+.01	15.36	-.04
28	13.79	-.06	09.31	-.16
30	22.13	-.01	03.51*	-.14
32	30.49	+.01	43097.85	-.05
34	38.85	+.00	92.29	+.04
36	47.20	-.02	86.63*	-.07
38	55.86	+.10	81.26*	+.02
40	64.37	+.10	75.98	+.12
42	72.90	+.09	70.73	+.14
44	81.44	+.05	65.34	-.07
46	89.99	+.01	60.31*	+.00

J	$^2F''(J)$ Phillips 3,1	4,1	$^1\Sigma - ^1\Sigma$ 1,1
1	10.79		10.7
3	24.95		25.11
5	39.49	39.45	39.40
7	53.79	53.75	53.79
9	67.99		68.09*
11	82.41	82.36	82.51*
13	96.74	96.68	96.67
15	111.01	110.96	110.95
17	125.32		125.16
19		139.43	139.47
21		153.55	153.40*
23			167.94*
25		181.96	182.02
27		196.01	196.30
29			210.28*
31			224.28
33			238.20
35			252.22*
37			266.02*
39			279.88
41			293.64
43			307.56
45			321.10*
47			334.57

TABLE 2 (continued)

J	R(J)	o - c	P(J)	o - c	J	$\Delta_2F''(J)$ Phillips 3,1	4,1	$^1\Sigma - ^1\Sigma$ 1,1
48	98.61	+.02	55.42	+.12	49			348.25m
50	43407.24	+.02	50.36m	-.01	51			361.91m
52	415.77	-.09	45.33m	-.20	53			375.77
54	24.61	+.10			55			
56	33.08	-.08			57			
58	41.75	-.06			59			
60	50.25	-.19			61			
62	58.95	-.12			63			
64	67.50	-.17			65			
66	76.08	-.16			67			
68	84.87	+.07			69			
70	93.17	-.02			71			
72	43501.70	-.08			73			
74	10.19	-.02			75			
76	18.61	+.03			77			
78	26.72m	-.17			79			
80	35.50m	+.37			81			
82	(43.33)				83			
84	(51.39)				85			
86	(59.86)				87			
88	(67.42)							

TABLE 3

2 - 2 Band

J	R(J)	o - c	P(J)	o - c	J	Phillips 5,2	$\Delta_2F''(J)$ $^1\Sigma-{}^1\Sigma$ 2,2	mean
0								
2	43186.24	-.08	43168.64*	+.18	1			
4	93.65	+.05	61.51	+.05	3			
6	43200.99	-.03	54.50	-.04	5	39.01	39.15	39.08
8	08.36	-.03	47.84	+.12	7	53.48	53.15	53.32
10	15.83	-.07	40.90*	-.06	9	67.32	67.46*	
12	23.45	-.02	34.35	+.05	11	81.54	81.48	
14	31.09	-.05	27.76*	+.02	13		95.69*	
16	38.86	+.01	21.35	+.10	15		109.74*	
18	46.77	+.13	14.81	-.05	17		124.05	124.05
20	54.45	-.02	08.50	-.06	19		138.27	138.27
22	62.31	-.07	02.29	-.04	21		152.16	152.16
24	70.42	+.08	43096.24	+.04	23		166.07	166.07
26	78.31	-.04	90.16	-.01	25		180.26	180.26
28	86.38	-.05	84.35*	+.09	27		193.96*	
30	94.43	-.11	78.36*	-.01	29		208.02*	
32	43302.62	-.09	72.66	+.04	31		221.67	221.67
34	10.89	+.00	66.97	+.06	33		235.65	235.65
36	19.16	+.03	61.39	+.07	35		249.50	249.50
38	27.42	+.02	55.84	+.09	37		263.32	263.32
40	35.68	-.04	50.36*	-.02	39		277.06*	
42	44.16	+.10	45.33*	+.26	41		290.35*	
44	52.48	+.05	40.00	+.14	43		304.16	304.16
46	60.80	+.01	34.90*	+.23	45		317.58	317.58
					47		331.11	331.11

TABLE 3 (continued)

J	R(J)	o - c	P(J)	o - c	J	Phillips $^1\Sigma - {}^1\Sigma$ 5,2	$\Delta_2 F''$ (J) $^1\Sigma - {}^1\Sigma$ 2,2	mean
48	69.18	+.00	29.69	+.10	49	344.46	344.46	
50	77.77	+.19	24.72	+.13	51			
52	85.96	-.04	(19.89)		53			
54	94.37	-.03	(14.37*)		55			
56	43402.80	-.02	(09.54)		57			
58	10.95*	-.29			59			
60	19.72*	+.09			61			
62	27.95	-.04			63			
64	36.72	+.37			65			
66	44.65	-.03			67			
68	53.02	+.05			69			
70	61.42	+.20			71			
72	69.45	+.01			73			
74	77.63	-.01			75			
76	(84.91)				77			
78	94.24				79			
80	43501.70				81			
82	10.19*				83			
84	18.61*				85			
86	26.72*							

TABLE 4

3 - 3 Band

J	R(J)	o - c	P(J)	o - c	J	$\Delta_2 F''$ (J)
0	43154.50	+.11				
2	61.51*	+.00	43143.84		1	
4	68.64*	-.05	36.89		3	24.62
6	76.03	+.07	30.11		5	38.53
8	83.19	-.10	23.43*		7	52.60*
10	90.69	+.00	16.63		9	66.56
12	98.28	+.13	09.88		11	80.81
14	43205.61*	-.07	03.51*		13	94.77*
16	13.38	+.12	43097.04	+.00	15	108.57*
18	20.90	-.02	90.67	-.02	17	122.71
20	28.74	+.12	84.35*	-.05	19	136.55*
22	36.49*	+.10	78.36*	+.13	21	150.38*
24	44.22	+.10	72.13*	+.01	23	164.36*
26	52.19	+.16	66.21	+.09	25	178.01
28	60.16	+.30	60.31*	+.11	27	191.88*
30	68.38*	+.11	54.47	+.10	29	205.69
32	76.10	+.09	48.75	+.03	31	
34	84.13*	-.07	43.13	+.16	33	
36	92.07*	-.19	37.47	+.07	35	
38	300.07*	-.11	32.13	+.20	37	
40	08.33*	-.09	26.59	+.04	39	
42	16.54*	-.08	21.52*	+.25	41	
44	24.81*	+.09	16.19	+.09	43	
					45	

TABLE 4 (continued)

J	R(J)	o - c	P(J)	o - c	J	$\Delta_2 F''(J)$
46	33.20*	+.15	10.85	-.10		
					47	
48	41.54*	+.35				
					49	
50	50.03*	+.00	01.01	-.01		
					51	
52	58.00	-.01	42996.00	+.19		
					53	
54	66.31	-.13				
					55	
56	74.53	-.06	86.85	+.05		
					57	
58	82.93	+.17				
					59	
60	(90.51)	-.15				
					61	
62	99.55					

TABLE 5

4 - 4 Band

J	R(J)	o - c	P(J)	o - c	J	$\Delta_2 F''(J)$
0						
2	43138.57	-.10	43121.35*	+.16	1	
4	45.87	+.09	14.49	+.15	3	24.08
6	53.06	+.08	07.51	-.04	5	38.30
8	60.26	+.02	00.87	+.00	7	52.19
10	67.53	-.03	94.27	+.03	9	65.99
					11	79.83
12	74.89	-.06	87.70	+.00		
14	82.38	-.05	81.26	+.01	13	
16	89.93	-.02	74.88	-.01	15	107.50
18	97.59	+.04	68.57	-.05	17	121.36
20	43205.22	+.03	62.60*	+.18	19	
22	13.38*	+.48	56.13d	+.19	21	
24	20.62	-.05			23	
26	28.44	-.05	44.34d	+.04	25	
28	36.49*	+.14	38.56	+.02	27	
30	34.22*	-.09	32.75	-.07	29	
32	52.19	-.11	27.17d	+.02	31	
34	60.16*	-.17	21.52d	-.14	33	

TABLE 6

5 - 5 Band

J	R(J)	o - c	P(J)	o - c	J	$\Delta_2 F''(J)$
2	43119.19	-.09				
					3	24.02
4	26.26	-.06	43095.17			
					5	37.78
6	33.49	+.10	88.48			
					7	
8	40.66	+.04	*			
					9	65.27
10	47.84*	-.02	75.39			
					11	79.01
12	55.18d	+.01	68.83*			
					13	92.58
14	62.56	+.00	62.60*			
					15	106.43
16	69.82	-.19	56.13*			
					17	120.09
18	77.53	+.00	49.73			
					19	133.19
20	85.16*	+.28	*			
					21	146.94
22	92.79	+.07	38.22*			
					23	160.66
24	43200.63	+.42	32.13*			
					25	
26	08.36*	+.20				
					27	
28	15.83*	-.13				
					29	
30	23.78	-.04				
					31	
32	31.91	+.19				
					33	
34	(39.68)	+.00				
					35	
36	48.02	+.32				
					37	
38	56.03	+.28				
					39	
40	63.95	+.09				
					41	
42	72.20	*.19				
					43	
44	83.99					

TABLE 7

0	43226.97	1.81171_3	1.82372_1	7.1475	7.4815
1	43201.17	1.7939_3	1.8049_4	7.190	7.518
2	43175.52	1.7757_8	1.7858_9	7.233	7.530_5
3	43150.86	1.7558_0	17651_9	7.50	7.67
4	43128.13	1.7380_5	1.7474_4	7.5	7.5
5	43108.86	1.719_9	1.729_{51}	7.5	7.5

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